REPORT NO. 8 (INTERIM REPORT)
GEORGIA TECH PROJECT NO. A-680

15 February 1963 to 15 February 1965

QUARTZ CRYSTAL AGING EFFECTS

By R. B. Belser and W. H. Hicklin

CONTRACT NO. DA-36-039-AMC-02251(E)
PROJECT NO. 1P6-22001-A-058-01-07

PREPARED FOR THE U. S. ARMY ELECTRONICS LABORATORY
FORT MONMOUTH, NEW JERSEY

15 February 1965

Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

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Placed by the
U. S. Army Electronics Laboratory
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I. PURPOSE

The purpose of this research is to reduce the aging and failure rates of quartz resonators, thereby increasing their reliability. The investigation will examine the effects of various materials, fabrication techniques, and operating conditions on aging and reliability; the effects of exposure to selected types of radiation, principally gamma radiation, will be determined. In addition, low frequency units of 100 to 500 kc frequency range are to be examined.

Of particular interest is the effect of the differences among the various types of quartz (natural, swept natural, cultured, and swept cultured quartz) on the long term aging of resonators and on the differences in behavior of the various resonators after irradiation.

Methods of x-ray diffraction topography are to be applied in examination of units to determine the incidence of imperfect structure, twinning, and strains in the variously fabricated units and to correlate these where possible with resonator aging and reliability.

II. ABSTRACT

The purpose of this research is to improve the aging and reliability of quartz resonators.

Approximately 325 quartz resonators have been fabricated or purchased and measured for aging and reliability at 85°C over periods up to 14 months. These have been divided among low frequency (100 to 500 kc), 3 Mc, 10 Mc and 16 Mc resonators and among natural, cultured, and electrolytically swept natural and cultured quartz. Data accumulated by electrical measurements and by visual and x-ray diffraction methods have been analyzed in order to determine mechanisms responsible for the principal aging vectors observed. Measured reliabilities are reported.

Of 96 low frequency resonators only 46 percent passed the initial aging requirement of < 5 ppm during the first 30 days. Three of these failed the subsequent requirement of < 2 ppm each 30 days thereafter giving a reliability of 94% for a 6 month period. Analyses by x-ray diffraction methods revealed strains associated with the quartz blank fabrication and mounting methods. Edge grinding, silver spotting, plating separation by airbrasive, quartz defects, and strained mounts, all appeared as possible contributors to high positive aging rates.

A comparison of the aging rates of 3 Mc resonators constructed of natural, natural swept quartz, cultured and cultured swept quartz was made, but inadvertently at the third inharmonic response in z' rather than at the fundamental. At this response, after <u>20</u> weeks, rates were $< 3 \times 10^{-9}$/wk for all except the cultured quartz which remained slightly $> 1 \times 10^{-8}$/wk. A comparison of the aging at the fundamental (3.00 Mc) and third inharmonic (3.22 Mc) responses revealed that the 3.22 Mc response was more temperature sensitive (about 1.2 ppm/°C) than the 3.00 Mc response but aging rates were little different over a 15 day period.

Ten Mc AT-cut resonators, fabricated for reliability and cement bond evaluation studies, were examined. Of 27 units 100 percent reliability was maintained for 11 months, based on an aging rate of $< 1 \times 10^{-7}$/wk. Two units became erratic and at 14 months reliability was 92.6%. Aging rate for better units at this time did not exceed $\pm 1.2 \times 10^{-8}$/month. Concurrently, of 68 10 Mc resonators, bonded with various cements and examined for cement bond evaluation studies, 86% and 91% respectively passed the initial and subsequent aging requirement of $< 1 \times 10^{-7}$/wk. After temperature cycling to 300°C frequency shifts up to 10×10^{-7} were common; however 41% shifted $< 5 \times 10^{-7}$. Aging rates subsequent to temperature cycling were little changed. Bondmaster bonded resonators withstood the temperature cycling with the least frequency change; however Pyroceram bonded units gave uniform frequency changes in a positive direction. Drive sensitivity was found related to aging and to resonator performance with various cements. Resonator etch techniques were developed which improved drive sensitivity, aging, and cement performance.

16 Mc AT-cut resonators fabricated, aged, and exposed to gamma radiation doses of 10^4 rads at Georgia Tech (Cs-137 source) and at SPRF exhibited frequency changes of a few parts in 10^7, of the order of magnitude of changes incurred by control specimens exposed to the same thermal and mechanical experiences. Elements of cultured quartz exhibited definite small positive shifts, however, and natural quartz revealed slight negative ones. The swept cultured quartz was least affected as reported in previous experiments.

X-ray diffraction investigations of quartz made concurrently with aging studies have revealed strains due to edge grinding, scratches, silver spotting, plating separation, twinning, bonding cements, metal films,

internal defects, and twisting due to mounting systems. These have been associated where practicable with aging, principally among the low frequency units. For the AT-cut units the relation is less substantive but exists in some cases. Methods of x-ray diffraction analyses of vibrating modes of quartz crystals have been discussed and the normal mode of oscillation of the SL-cut crystal has been shown to be 3rd order face shear.

III. PUBLICATIONS, LECTURES AND REPORTS

A detailed statement of publications, reports, and conferences occurring during each quarter has been submitted in each succeeding Quarterly Report respectively. Publications other than those required by contractual agreement have been limited thus far to the papers presented at the 17th and 18th Annual Symposia on Frequency Control.[1,2,*]

During the eighth Quarter, Monthly Progress Letters Nos. 19, 20, and 21 covering the months of November and December, 1964, and January, 1965, were submitted. Quarterly Report No. 6 was distributed and the approval copy of Quarterly Report No. 7 was submitted. Mr. J. M. Stanley of USAEL visited the Georgia Institute of Technology on 20 November 1965, for conferences on technical phases of the research.

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[1] R. B. Belser and W. H. Hicklin, "Aging Characteristics of Quartz Resonators with Comments on the Effects of Radiation," "Proceedings of the 17th Annual Symposium on Frequency Control," Fort Monmouth, N. J. 1963, pages 127-175.

[2] R. B. Belser and W. H. Hicklin, "Aging Analysis of AT-Cut Quartz Resonators of Natural, Cultured, and Swept Varieties," "Proceedings of the 18th Annual Symposium on Frequency Control," Fort Monmouth, N. J., May 1964, pages 129-165.

[*] A. L. Bennett, R. A. Young, and N. K. Hearn, Jr., "X-ray Diffraction Topography of Vibrating Quartz Crystals, Applied Physics Letters 2, No. 8, 154-156, April 15, 1963.

IV. FACTUAL DATA

A. INTRODUCTION

This research has been concerned with six principal areas of investigation related to quartz resonators during a period of two years. These were:

1. The aging of low frequency resonators (100 kc to 500 kc);
2. The aging of 3 Mc AT-Cut resonators fabricated of various types of quartz;
3. The aging of 10 Mc AT-Cut resonators fabricated for reliability measurements;
4. The aging of 10 Mc AT-Cut resonators fabricated for bonding cement evaluation studies;
5. The aging of 16 Mc AT-Cut resonators fabricated for radiation effect studies; and
6. The application of x-ray diffraction techniques in quartz resonator aging analyses.

Since each phase has been covered at great length in successive quarterly reports, and in much more detail than possible in a single summary report without undue length, this report will be restricted to short summaries of the results of each study. References are made to the more complete detailed studies, and a more extensive treatment of data obtained during the eighth quarter.

Data obtained during the latter quarter has been principally concerned with a continuation of the cement-bond-evaluation studies and further aging analyses of resonators by x-ray diffraction and other methods.

B. APPARATUS

1. General

The apparatus for aging studies consisted principally of storage ovens controlled at 85°C ± 0.01°C and the frequency measuring apparatus utilizing a frequency synthesizer and a bridge for passive drive of the units. The method used has been described in detail in Quarterly Report No. 1 of this Contract, dated 15 May 1963. Measurement accuracy is a few parts in 10^9 but the principal limiting factor in accuracy has been the oven stability and occasional problems with the mercury thermostats employed. In the early portion of the work a Rohde and Schwarz Frequency Synthesizer, Model XUA, was used and subsequently a Hewlett Packard Unit, Model 5100 (obtained about 1 June 1964) was utilized.

The apparatus for resonator fabrication and sealing are vacuum chambers based on standard Pyrex Pipe forms that have been especially adapted for the job.[3] Plating was deposited simultaneously on both sides of the quartz, which was maintained at a temperature of 350°C, by radiant heaters within the chambers. Overcoating to frequency was employed only for units that were being included in the 10 Mc reliability series.

The x-ray diffraction apparatus employed was described in the Final Report (No. 8) of Contract No. DA-36-039-SC-87407 and has been previously described elsewhere as well.[3,4]

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[3] R. B. Belser and W. H. Hicklin, "Aging Characteristics of Quartz Crystal Resonators," Final Report Contract No. DA-36-039-SC-87407, 15 February 1963.

[4] R. B. Belser and W. H. Hicklin, "Aging Characteristics of Quartz Crystal Resonators," Quarterly Report No. 6, Contract No. DA-36-039-SC-87407, 15 August 1962.

The apparatus consisted of two types. In one, a broad beam x-ray source is collimated by a Soller slit (consisting of a series of closely spaced parallel plates of several inches length), thereby establishing parallelism and character to the beam. The beam falling on a quartz plate at the proper Bragg angle is diffracted to a film upon which the various intensities are registered. An image of the crystal plate is formed, upon which are superimposed the shadows of the plates of the Soller slit. A distortion of the image of the multiple slits indicates distortion of the quartz plate. Lattice and other defects are usually visible as zones of intensity different from that of the plate average. This method has been named by Dr. Young of our staff as the Source Image Distortion (SID) Method.[1,4] The second method utilizes Lang Topography.[5] In this method the quartz plate and the film, properly positioned, are translated across the beam at a suitable rate to give proper exposure to the film. Lang Topography registers differences in intensity caused by any disturbance creating gradients or abrupt changes in lattice spacing; hence, dislocations, flaws, twinning, impurity bands and surface damage may be detected. Also strain gradients and crystal plane deflections associated with piezoelectric or acoustic oscillations may be detected and examined. The SID technique displays the listed topographic features with somewhat less resolution in addition to the plate distortion effects.

2. Aging of Low Frequency Resonators (100 to 500 kc)

Ninety-six low frequency quartz resonators were obtained from commercial sources, 32 from each of three manufacturers. These were divided among frequencies and cuts as follows:

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[5] A. R. Lang, "Studies of Individual Dislocations in Crystals by X-ray Diffraction Microradiography," Journal of Applied Physics 30, 1748 (1959)

Frequency	Number of Units	Type of Cut
100 kc	24	NT
250 kc	24	CT
455 kc	24	CT or DT or SL
500 kc	24	CT or DT or SL

After suitable preliminary measurements the operable units (85) were placed in 85°C ovens for aging measurements and these were conducted for a period of 180 days.

The specifications called for these units to age not more than 5 ppm during the first 30 days nor more than 2 ppm for each 30 days thereafter. Table 1 lists the results of the aging measurements at the end of 110 days and this aging rate continued essentially unchanged for a period of 180 days, only 47 (55%) units passed the acceptance requirement. Only three of these failed the subsequent requirement of < 2 ppm/month giving a reliability of 94%. The yield of passing units with respect to the initial number, 44/96 (46%) was poor. However, 17 additional units failed the initial requirement but passed the subsequent one of $< 2 \times 10^{-6}$ per month. These could have been included if a 60 day aging specification had been adopted.

Subsequent to the aging measurements the units were leak tested by the vacuum oil method[6] and selected units were disassembled for inspection and x-ray diffraction examination. The fabricators of the low frequency resonators were visited to discuss processes which might contribute to the initially high

[6] R. B. Belser and W. H. Hicklin, "Study of Aging Effects of Quartz Crystal Plates," Final Report, Contract No. DA-36-039-SC-74946, USASEL, Ft. Monmouth, N. J., July 31, 1958.

TABLE 1

RELIABILITY STUDY LOW FREQUENCY RESONATORS

Classification XX (Poor, Poor)	XV (Poor, Good)	VX (Good, Poor)	VV (Good, Good)	
A-100-6	A-100-3		A-100-2	
A-100-8	B-100-1		B-100-2	
B-100-6	B-100-3		C-100-2	
B-100-7	B-100-4		C-100-5	
C-100-3	B-100-8		C-100-7	
	C-100-1			
	C-100-6			
	C-100-8			
B-250-1	B-250-2	A-250-4	A-250-1	
B-250-3	C-250-3		A-250-2	
B-250-4	C-250-4		A-250-3	
B-250-5	C-250-5		A-250-5	
B-250-6	C-250-6		A-250-6	
B-250-7	C-250-7		A-250-7	
B-250-8	C-250-8		A-250-8	
C-250-2			C-250-1	
A-455-1	B-455-7	B-455-2	A-455-5	C-455-6
A-455-2	B-455-8		A-455-7	C-455-7
A-455-3(?)			B-455-1	C-455-8
A-455-4			B-455-3	
A-455-6			C-455-3	
B-455-4(?)			C-455-4	
B-455-5			C-455-5	
B-455-6				
		B-500-3	A-500-1	B-500-7
			A-500-2	B-500-8
			A-500-3	C-500-1
			A-500-4	C-500-2
			A-500-5	C-500-3
			A-500-6	C-500-4
			A-500-7	C-500-5
			A-500-8	C-500-6
			B-500-2	C-500-7
			B-500-5	C-500-8
			B-500-6	
Totals 21	17	3	44	

RELIABILITY: 44/47 = 93.6%

* The first indicator refers to the first 30 days acceptance test; the second to subsequent aging. First 30 days: < 5 ppm. Subsequent: < 2 ppm/30 days.

(Continued)

TABLE 1 (Continued)

Summary

Distribution of Resonators by Frequency

Frequency	XX	XV	VX	VV	Totals
100 kc	5	8	0	5	18
250 kc	8	7	1	8	24
455 kc	8	2	1	10	21
500 kc	0	0	1	21	22
	—	—	—	—	—
Total	21	17	3	44	85

Distribution by Fabricator

	XX	XV	VX	VV	Totals
Manufacturer A	7	1	1	18	27
Manufacturer B	12	7	2	8	29
Manufacturer C	2	9	0	18	29
	—	—	—	—	—
Totals	21	17	3	44	85

positive aging vectors. These were principally responsible for the failure of the units to pass the initial specification of $< 5 \times 10^{-6}$ during the first thirty days.

X-ray diffraction examinations of selected resonators by both the SID and Lang techniques revealed strains, defects, edge and surface damage occurring in some units. These observations were discussed with fabricators at the time of visits to their plants. It was apparent that methods of finishing to frequency by abrading edges, methods of separating electrodes into two parts on 100 kc units by sand blasting, and silver spot firing were inducing some undesired strains. In addition occasional twisted units, as shown in Figure 1 for 100 kc unit B-7, were observed. The figure also exhibits the strain line introduced by the airbrasive removal of a portion of the plating and a strain zone about the lower mounting pin. Edge strain is also slightly visible. Figure 2 exhibits the aging data for this unit (B-7). Figures 3 and 4 exhibit the SID pattern and aging data respectively for a second unit which apparently has intrinsic growth defects. More extensive investigations of these units and similar ones are outlined in the preceeding Quarterly Reports of this research, Nos. 5, 6, and 7.

It was evident from our visits to the four manufacturers that careful procedures were being used in the fabrication of the low frequency resonators. However, some of the faults mentioned occurred in products of each of the manufacturers used for the experiment. It is evident that these faults can affect aging, and normally strain anneal would be expected to give positive aging. However, the degree assignable to any one factor has not been ascertained.

In observations of the oscillation patterns of low frequency units (See Quarterly Report No. 7) it is apparent that the edge surfaces are very active

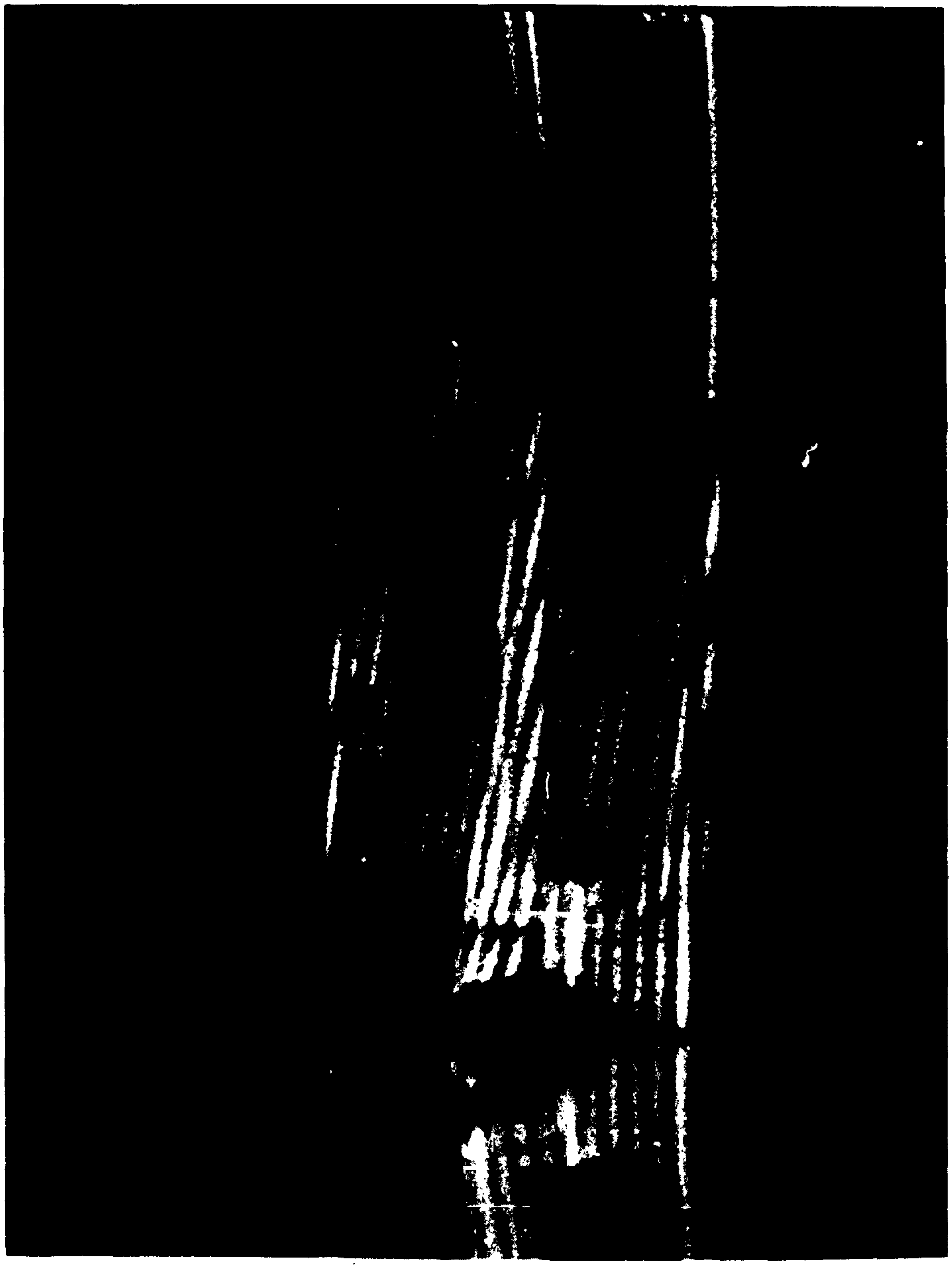

Figure 1. X-ray diffraction SID pattern of 100 kc resonator B-7 exhibiting twist in crystal and centerline strain zones.

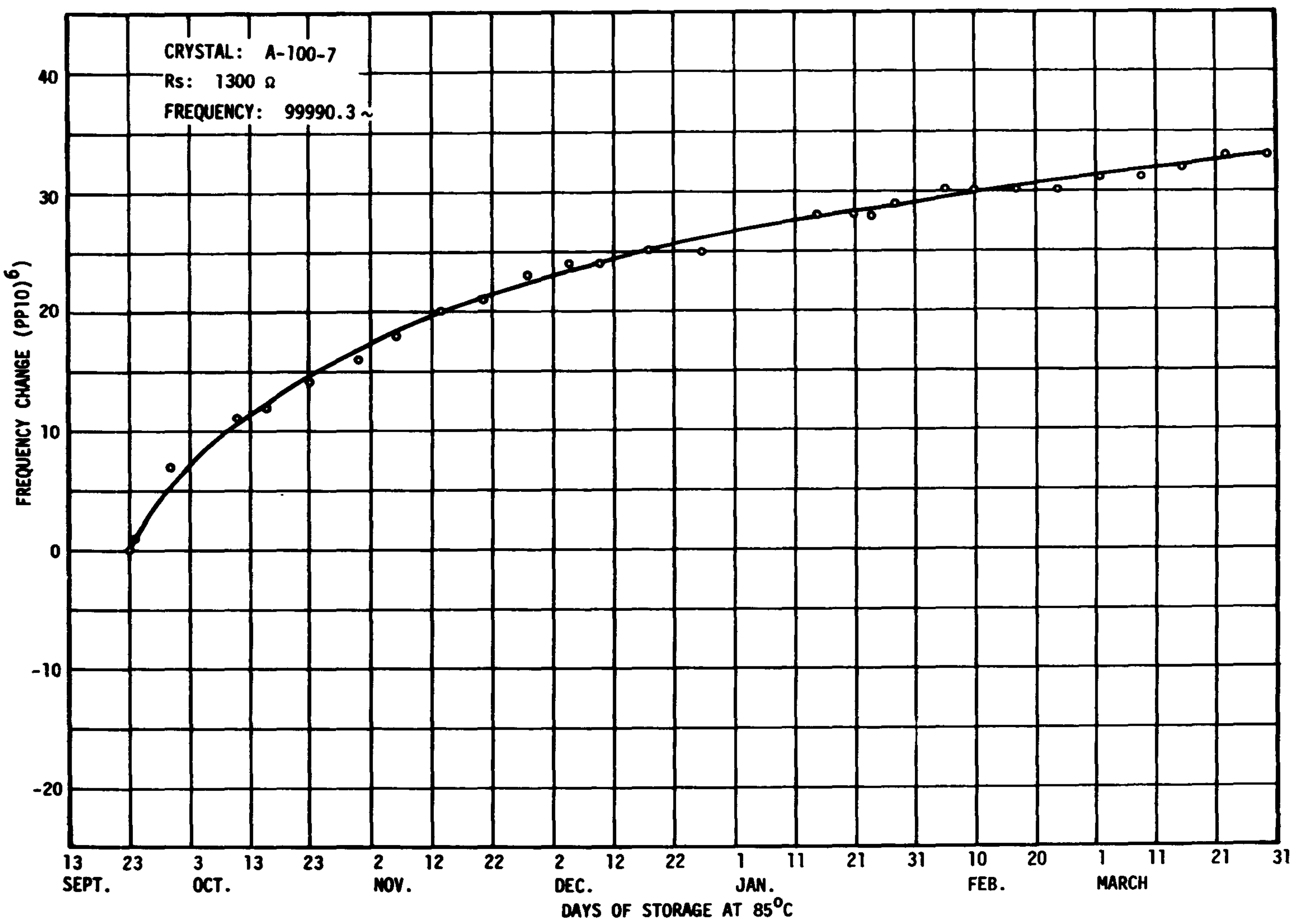

Figure 2. Aging data for 100 kc resonator B-7 (See Figure 1 preceding).

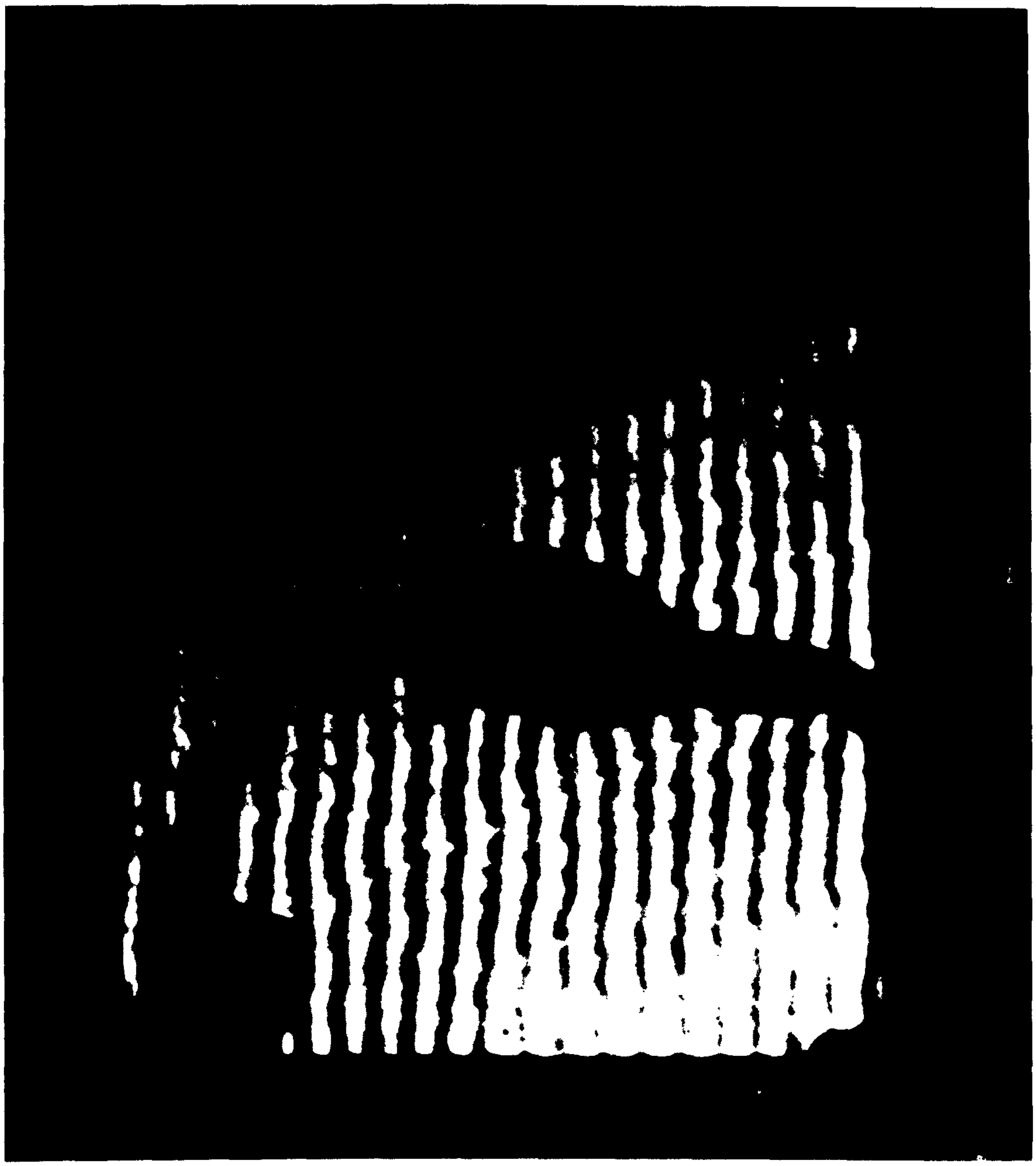

Figure 3. X-ray diffraction SID pattern of 455 kc resonator A-4, static; this unit appears to be of very imperfect structure and performed poorly.

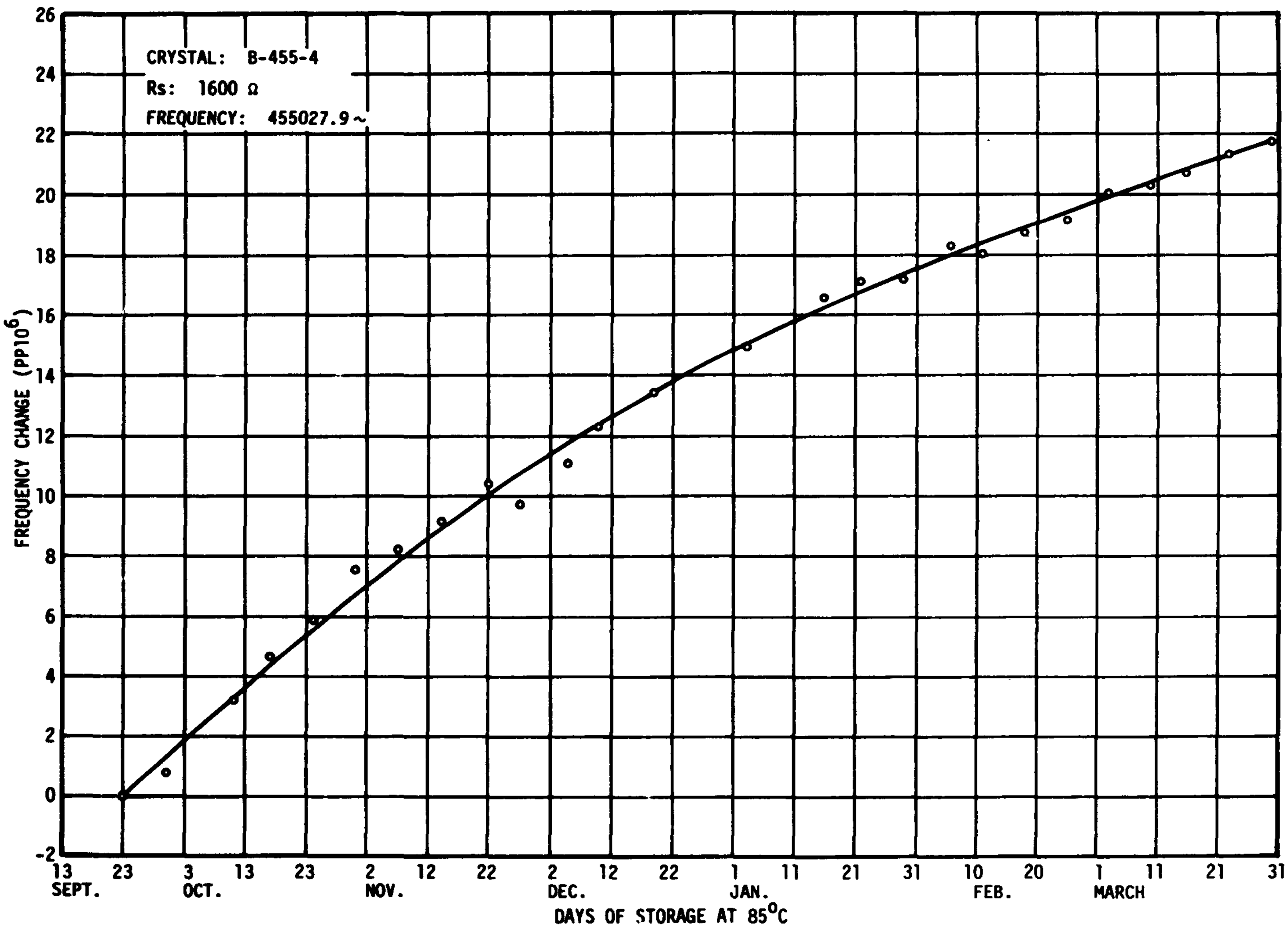

Figure 4. Aging data for 455 kc resonator B-4, (See Figure 3 preceding).

in the oscillation of the units. Hence, defects along the edge surfaces would be expected to play a considerable role in aging. Moreover, defects within the body of the quartz plate may upset the accuracy of location of nodes from the geometry of the plate, resulting in fired spots and mounting pins located slightly off the nodal position. Lastly, twists in the mounting assembly may contribute to aging.[7] In fact the annealing of strain in the usual metallic supports would be expected to proceed at a greater rate than annealing within the quartz. Studies are in course currently to isolate some of these factors by employing units with polished edges, no final frequency adjustment, thermal compression bonding, and no airbrasive separation of plating. It is believed that these will allow assessment of the relative aging effects ascribable to each of these variables.

3. Aging of 3 Mc AT-Cut Quartz Resonators

Twenty-four semi-precision AT-Cut 3 Mc quartz resonators were obtained from a supplier with the specification that 6 each be constructed of natural, swept natural, cultured, and swept cultured quartz. The frequencies of these units were measured at 85°C for a six-month period. Figure 5 gives aging data for typical units of each type of quartz. Figure 6 depicts the distribution of the aging data for the various types of quartz during 20 weeks of the experiment. Data of the last few weeks was discarded because of an oven-opening incident. It is apparent from Figure 6 that the majority of the resonators were within the bracket of $< 1 \times 10^{-8}$ frequency change per week toward the latter part of the experiment and that all except cultured quartz placed well with respect to the residual aging rate.

[7] R. J. Byrne and R. L. Reynolds, "Design and Performance of a New Series of Cold Welded Crystal Unit Enclosures," Proceedings of the 18th Annual Symposium on Frequency Control, Fort Monmouth, N. J., May 4-6, 1960, pp 166-179.

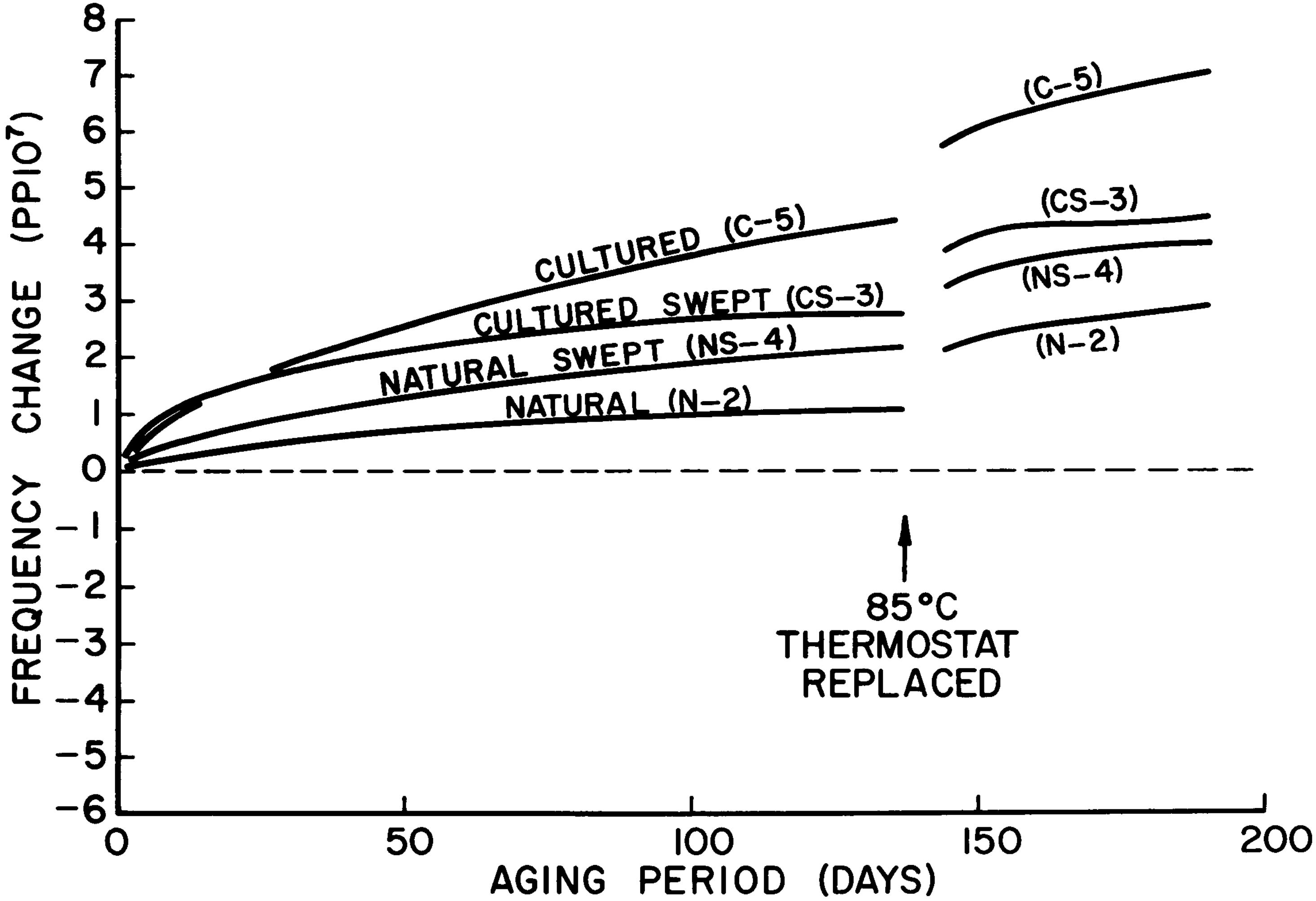

Figure 5. Aging data for typical AT-cut 3 Mc resonators of various types of quartz. (3.22 Mc response).

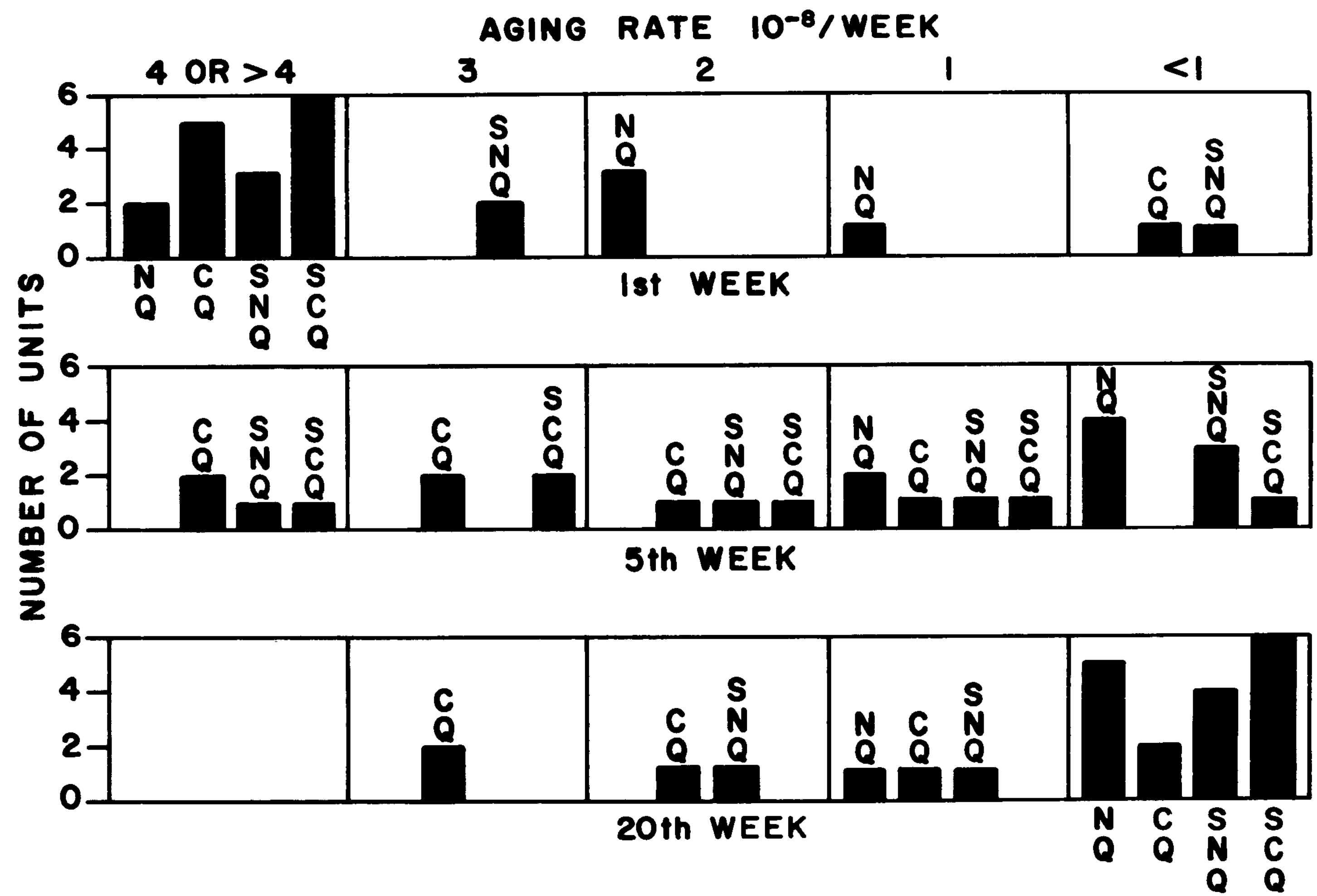

Figure 6. Aging distribution of 3 Mc resonators. (3.22 Mc response).

However, it was pointed out in Quarterly Report No. 7 that the data described above were inadvertently taken for the 3.22 Mc response, which turned out to be the 3rd inharmonic response along z', rather than the correct fundamental 3.001 Mc response. An immediate recheck of aging data for 8 units at the two responses was made and data for typical units are shown in Figure 7. It will be observed that the aging slopes at the 3.22 Mc responses are usually slightly different from those at the 3.001 Mc responses. Further a frequency versus temperature run for unit N-6 exhibits as shown in Figure 8 a large temperature coefficient of frequency, 1.2 ppm per $^{\circ}C$, or approximately 1.2×10^{-8} per $0.01^{\circ}C$. The turn-over temperature for the 3.001 Mc response, in addition, for this particular unit proved to be $75^{\circ}C$ instead of $85^{\circ}C$.

As a result of these remeasurements it was also determined that the 3.001 Mc and 3.22 Mc responses for these units were so strong and close together that the CI meter TS 330/TSM (Serial No. 2) used to drive them usually drove both modes simultaneously. We could only be sure of separation by a reduction of the voltage supplied to the CI meter (to as low as 43 volts) and by tuning to the desired frequency from a lower frequency. The frequency synthesizer and bridge, however, could be used to drive individually the correct response frequencies without difficulty.

The R_s obtained by the CI meter at line voltage was quite high (30 ohms) and obviously incorrect since the Z-dial on the frequency bridge gave a number equivalent to 6 to 8 ohms. The latter was essentially the number supplied by the manufacturer on request after the errors were discovered. Q calculations based on the early R_s measurements were incorrect. New values calculated were near 600,000 for the 3.001 Mc (fundamental) response and

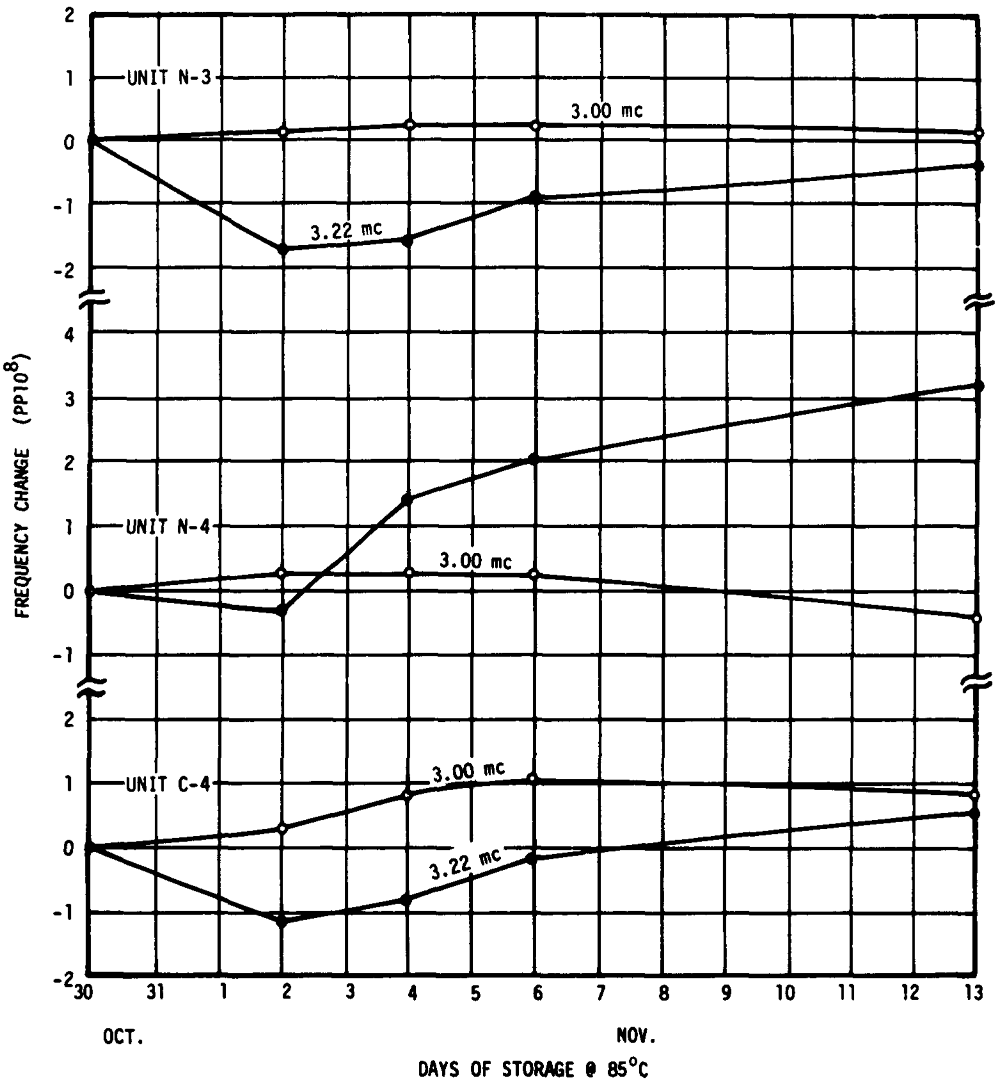

Figure 7. Aging data for 3 Mc resonators measured at 3.00 Mc and 3.22 Mc responses.

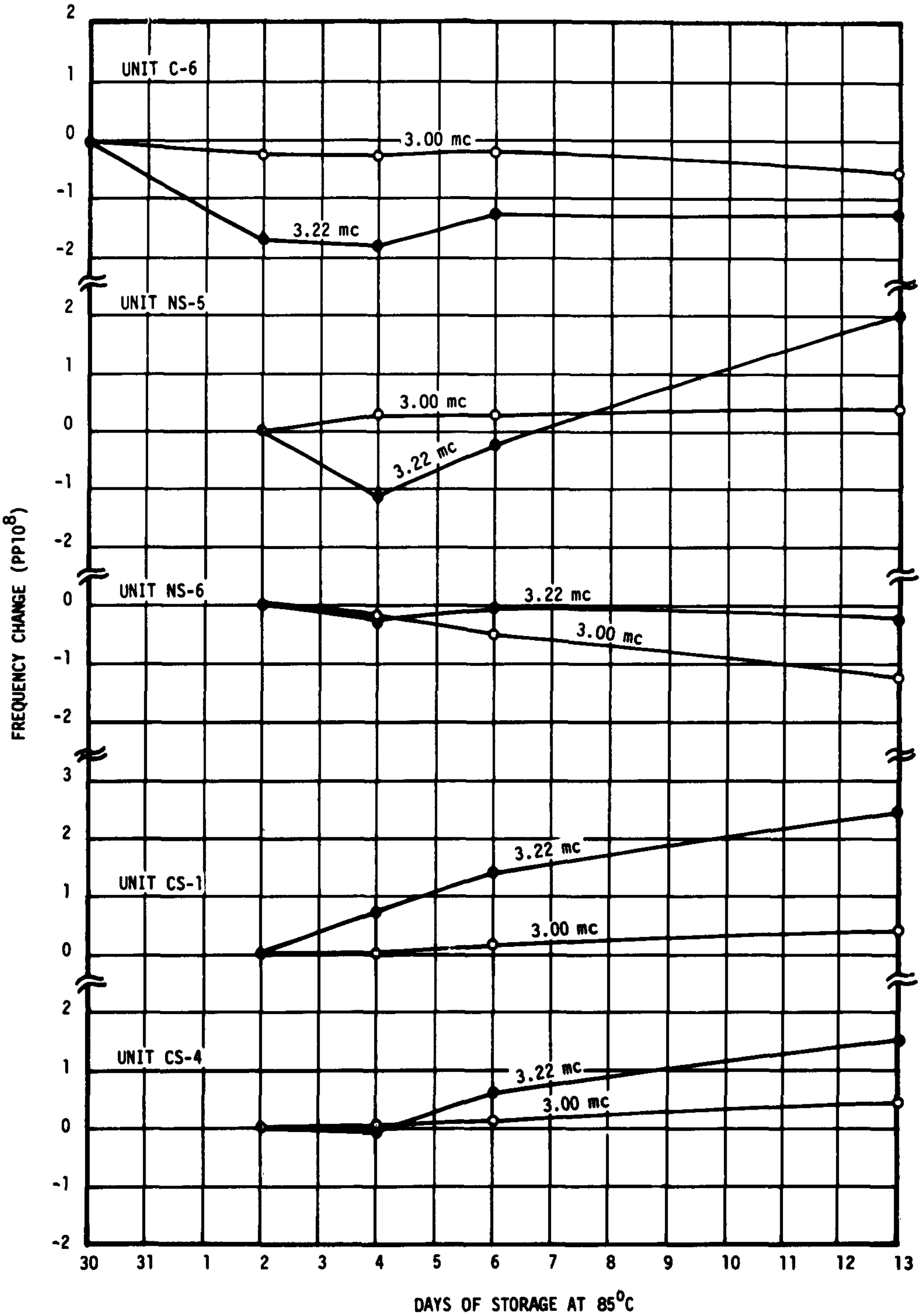

Figure 7 (Continued). Aging data for 3 Mc resonators measured at 3.00 Mc and 3.22 Mc responses.

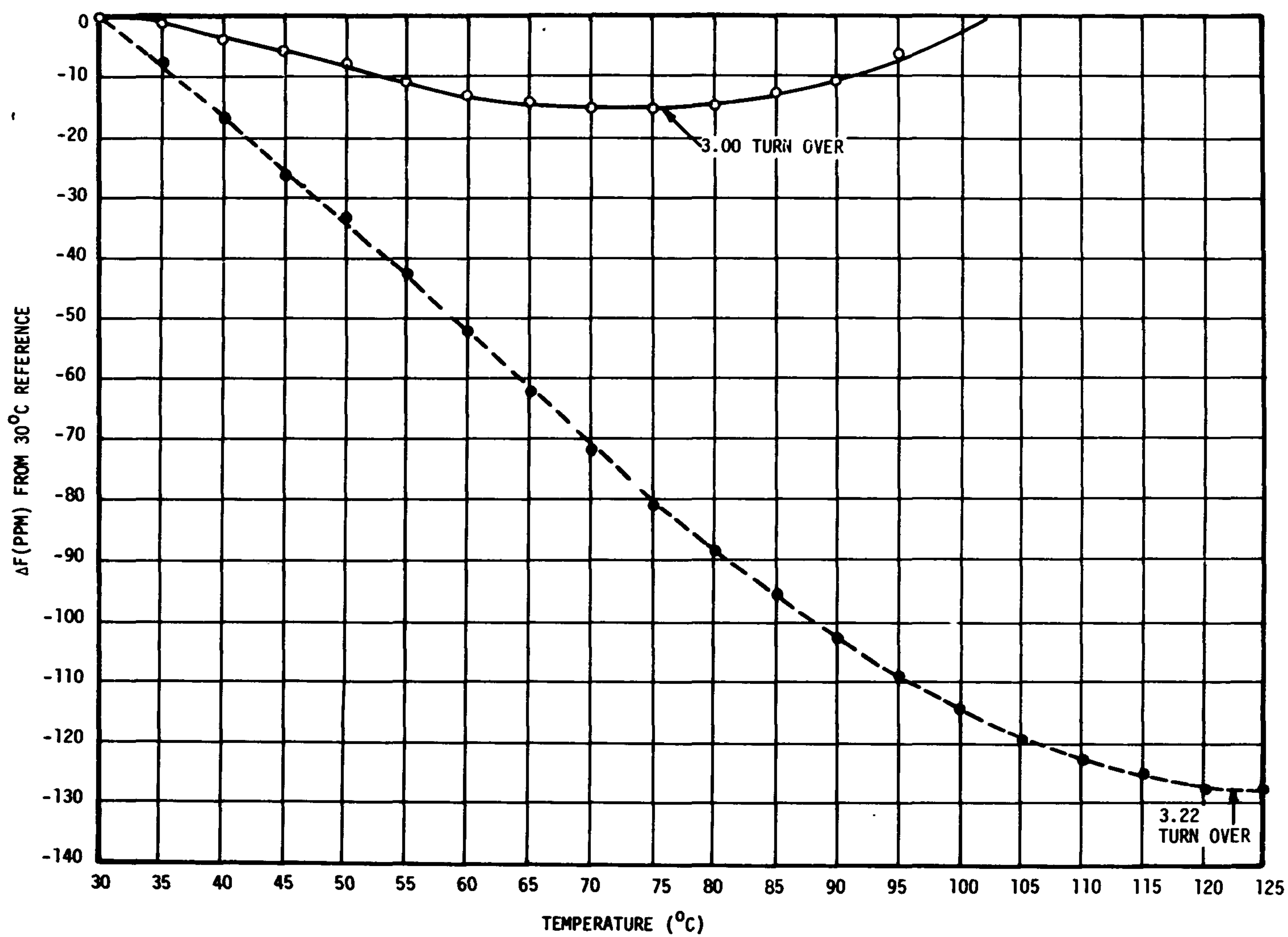

Figure 8. Temperature versus frequency data for natural quartz resonator N-6 at 3.00 Mc and 3.22 Mc responses.

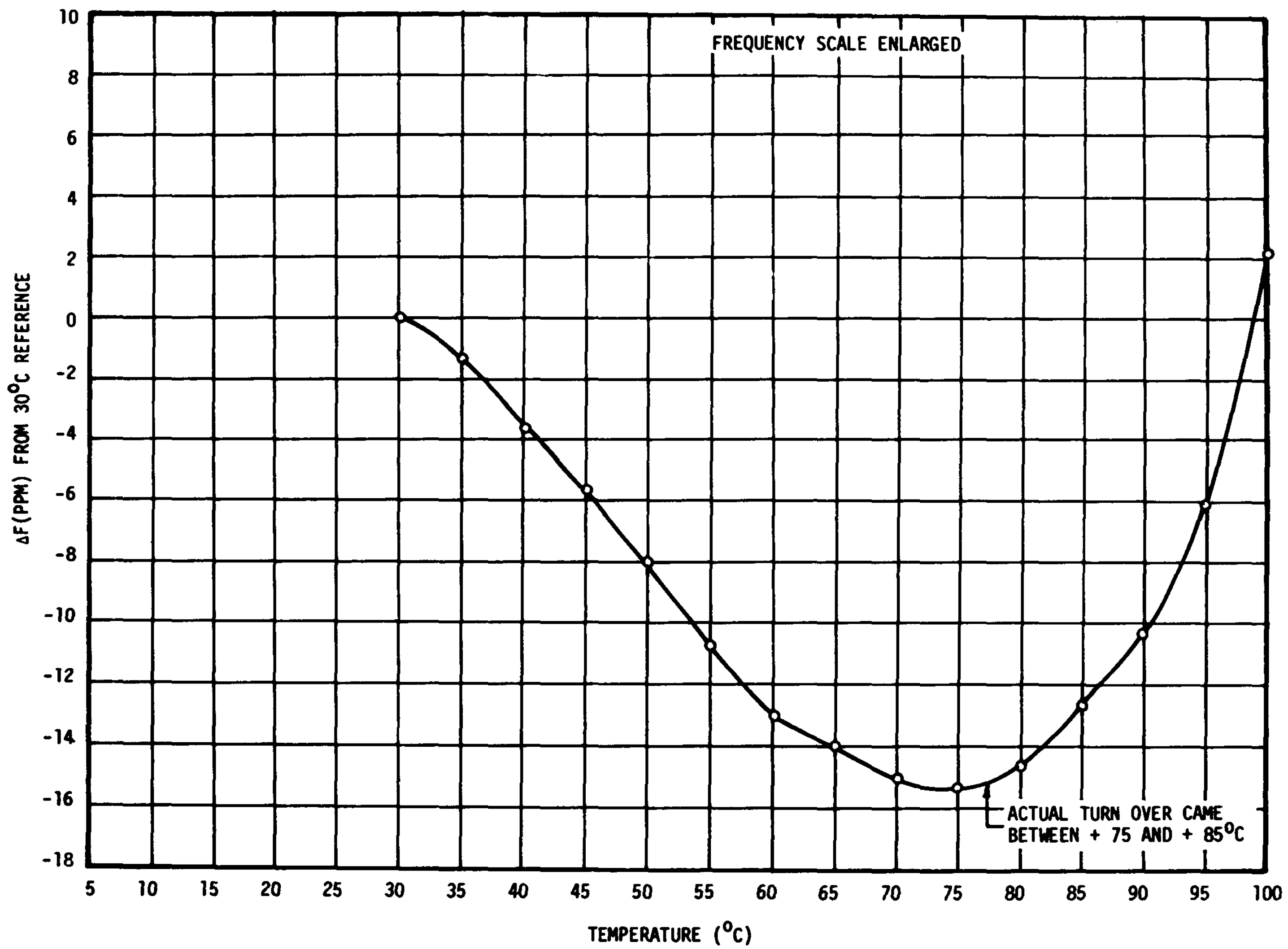

Figure 8 (Continued). Temperature versus frequency data for natural quartz resonator N-6 at 3.00 Mc and 3.22 Mc responses.

1,000,000 for the 3.22 Mc response. The Q for the latter response is higher than for the fundamental. Also the coupling between these modes, at even low drive levels, introduces difficulties that may be experienced in measuring correct R_s and Q values by prescribed methods.

The experiences with strong coupled modes in these units led us to examine the modes of motion of the units at the various responses with x-ray diffraction SID techniques. We were able to observe readily the 111, the 311, 131, 113 and 391 responses described by Roger Bennett[8] by powder techniques and by Koga[9] from data taken by the probe method. These were described in detail in our most recent Quarterly Report (No. 7). An example of the 113 mode (3.22 Mc) is shown in Figure 9. It is evident here that the vibrating portion is divided into 3 vibrating subportions; adjacent ones are approximately 180° different in phase. X-ray diffraction patterns using the 011 planes show a small amount of another mode present besides thickness shear, probably face shear. However, the latter appears to be stronger in the higher modes such as the (391).

An oblique pattern shown in Figure 10 was also observed at a frequency of 9.71 Mc. This pattern is almost identical to a powder pattern obtained by R. E. Bennett.[10] These studies indicate the complexities of the responses in a quartz plate and the need for a further investigation of them. The

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8 R. E. Bennett, "Quartz Resonator Handbook," Manufacturing Guide for AT-Type units, ASAEL (1960).

9 I. Koga, J. E. Rhodes, and W. B. Wrigley, "Quartz Crystal Studies and Measurements, Phase I," Final Report USAELRDL Contract No. DA-36-039-SC-78910, 1959.

10 R. E. Bennett, "Inharmonic Mode Powder Patterns (5.0 Mc Fundamental)," Informal Report Union Thermoelectric Division, Comptometer Corporation, Niles, Illinois (1960). (ASAEL Contract).

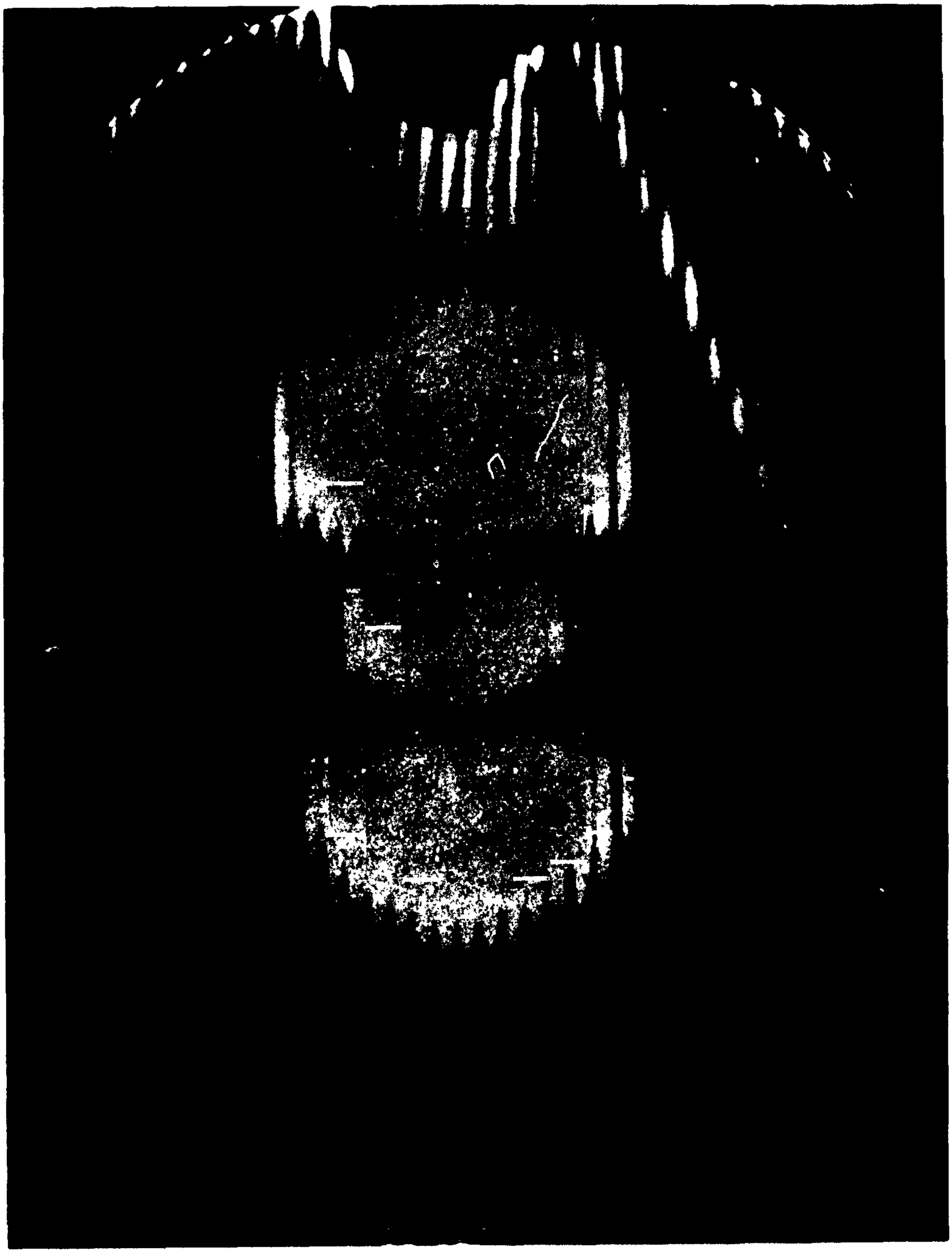

Figure 9. X-ray diffraction SID pattern of 3 Mc resonator N-6 oscillating in 113 mode, (3.22 Mc, 3rd. inharmonic in Z'), 60 volts to C.I. meter, ($2\bar{1}0$ reflection)

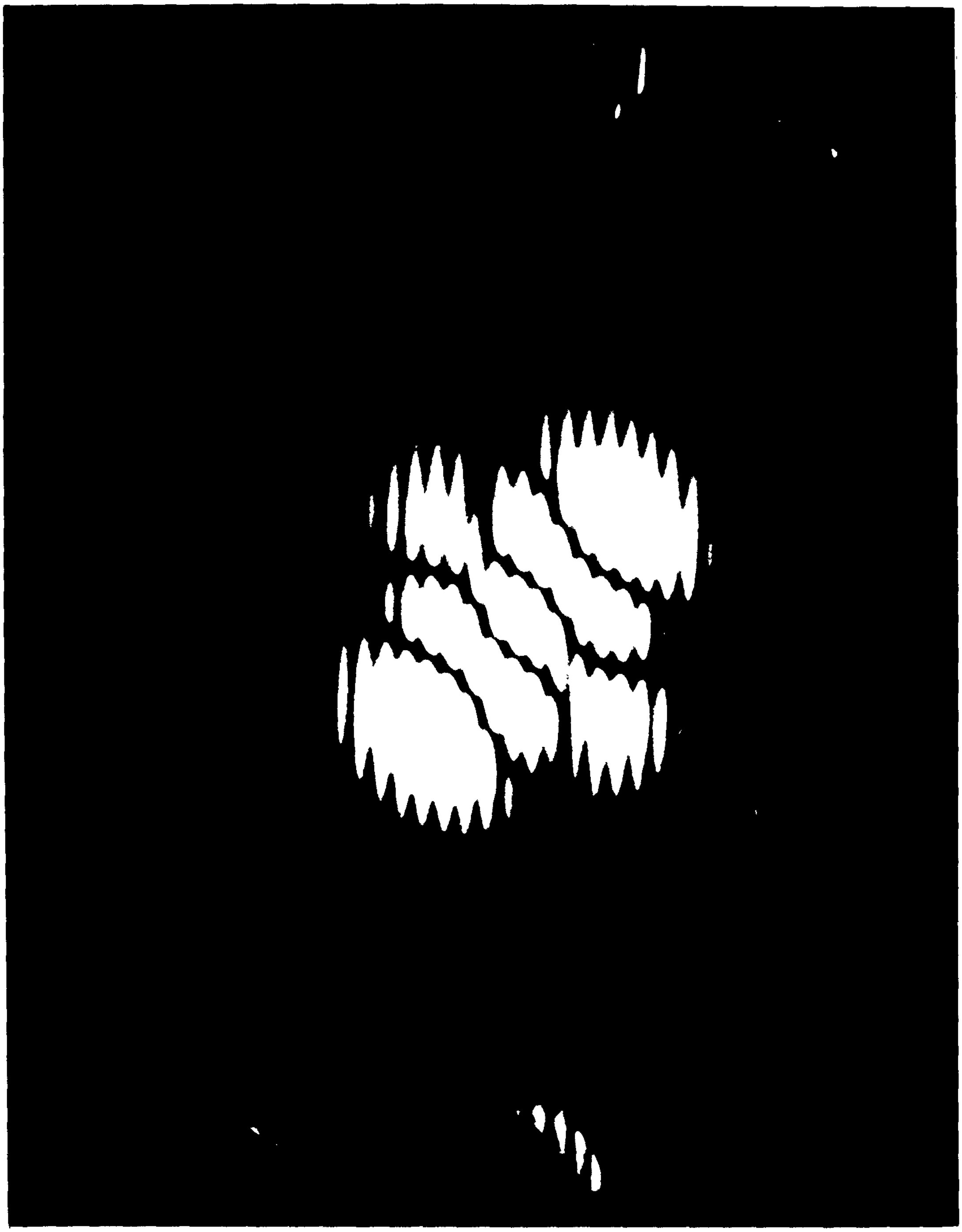

Figure 10. X-ray diffraction SID pattern of 3 Mc resonator NS-5 oscillating in oblique mode, (3,00,5), 9.22 Mc, ($2\bar{1}0$ reflection.)

x-ray diffraction method has proven to be a keen and non-destructive tool in mode analysis studies.

The validity of the aging results reported for the 3 Mc resonators may be questioned in view of the subsequent developments with respect to the 3.22 Mc response. However, the correlation between the 3.001 Mc and the 3.22 Mc response has been examined as pointed out in Figure 7. The results indicate that, if anything, the units are better than previously reported. Furthermore, the cultured quartz resonators are the only group for which data departed greatly from the average aging rate of the other groups at the end of the period. A further measurement of the aging of cultured quartz units at the correct response appears desirable.

4. Aging of 10 Mc Resonators for Reliability Measurements

In June 1963, 42 AT-Cut 10 Mc quartz resonators, plated with Au+Au, were fabricated for reliability studies. Twenty of the units were mounted in T 5 1/2 containers using du Pont 5504-A cement for bonding the spring clip to the resonator. The balance of 22 units were mounted in the HC 27/U glass container. One half of the latter units were bonded with Pyroceram-Silver (1/2) and the other half with du Pont 5504-A cement. Tabs instead of spring clips were used for the latter two groups (C and D).

Only 39 of the units were considered satisfactory for installation in the 85°C oven for aging studies. Two of these gave such erratic data that they were subsequently discarded; the balance of 37 furnished the basis for this study.

The aging continued for a total period of 14 months and was terminated after that in order to make an analysis of possible features contributing to

unusual aging behavior. Of the 37 units, 10 failed the initial specifications of an aging change < 4 ppm during the 1st 30 days at either the fundamental or 3rd mode measurement, leaving 27 resonators for the final reliability group. This represented a yield of good units of 27/42 or 64.2%. A large loss was suffered in group D in which only 2 of 11 units survived the acceptance test. The result undoubtedly was due in part to the use of du Pont 5504-A cement in the HC-27/U glass container, the sealing of which required exposure of the cement to undesirably high temperatures. For the first three groups the yield of acceptable units was 25/31 or 80.5%.

Of the 27 units continued on test for 14 months, two failed shortly after the end of the 11th month. Hence the reliability was 100 percent at the end of 11 months but only 92.6% at the end of 14 months.

The aging process of these units is described in great detail in Quarterly Reports 4, 6 and 7. Table 2 exhibits a final summary of the aging of the 27 units. The average aging of the good units at the end of 14 months was at a rate of $< \pm 1.2 \times 10^{-8}$ per month at both the fundamental and 3rd overtone. The extremes did not exceed $\pm 5 \times 10^{-8}$ per month. The aging curves of 60 percent possessed slightly negative slopes and 40 percent exhibited slightly positive slopes.

Approximately five months after the initiation of the aging measurements of these units the oven was opened and the ten unacceptable units were removed for examination by x-ray diffraction topography and by visual inspection. After 14 months the aging study was discontinued in order to inspect the remaining units before completion of the study phase. Results of this inspection, for the units examined, are tabulated in Table 3.

It is clear from the x-ray diffraction studies and visual examination of units, that there is quite a high incidence of surface flaws, internal

TABLE 2

AGING DATA FOR 10 MC AT-CUT QUARTZ RESONATOR RELIABILITY UNITS DURING A 14 MONTH PERIOD

	Aging						
	1st 30 days pp 10^8		Total pp 10^8		Last 30 days pp 10^8		
Resonator	1st mode	3rd mode	1st mode	3rd mode	1st mode	3rd mode	Remarks
T5 1/2 5504-A							
A-1	-37	-10	-103	-110	-2.5	-2.5	433 days-total aging time
A-3	-15	- 9	- 35	- 87	-3.0	-5.0	
A-4	-20	- 8	- 58	- 60	-1.0	-1.0	
A-6	-10	- 5	- 49	- 45	-1.0	-0.5	
A-7	-34	-29	- 88	- 98	-1.0	-1.0	
A-9	-12	+ 2	- 19	- 20	-1.0	-1.0	
A-10	- 2	-19	- 51	- 77	-1.0	-1.0	
T5 1/2 5504-A							
B-1	-20	- 9	- 53	- 62	-0.7	-2.1	
B-2	+ 6	+ 7	- 10	- 16	-0.5	-0.7	
B-3	- 2.5	- 2.9	- 58	- 74	-1.5	-0.5	
B-4	- 1.0	- 1	- 08	- 23	-1.0	-1.0	
B-5	-30	-16	- 45	- 49	-0.5	-0.5	
B-6	-39	- 3	+103	- 23	+0.7	-0.5	
B-7	- 9	+ 3	00	- 14	-1.0	-1.0	
B-8	-12	-23.5	- 39	- 84	-2.0	-3.0	
B-9	-32	-40			-2.0	-1.0	
B-10	-15	- 2	- 31	- 12	+0.5	+0.5	
HC 27/U Glass (Pyroceram)							
C-1	+29	+23	+ 65	+ 43	+1.0	+1.0	
C-2	-12	- 5	+ 71	+ 13	+1.0	+0.5	
C-3	+38	+10	+113	+ 23	+2.0	+0.5	
C-6	- 5	+ 3	- 0.6	- 15	+0.5	-0.5	418 days-last 2 measurements poor
C-9	+32	+ 1	- 11	- 31	+1.0	+0.5	Erratic at 180 days, but improved
HC 27/U Glass (Pyroceram)							
C-10	-11	- 2.5	- 0.1	- 54	+4.0	-1.0	fundamental split into two responses-330 days
C-11	+11	+17	+ 45	+ 35	+2.0	+2.0	Became erratic after 365 days
C-12	-16	- 6	- 20	- 45	+0.5	-1.0	
HC 27/U Glass 5504-A							
D-7	- 8	-34	- 51	- 89	+0.5	+0.5	
D-12	+13	+25	+ 23	+ 18	+0.5	0.0	355 days total period

TABLE 3

RESULTS OF INSPECTION OF 10 MC RELIABILITY RESONATORS BY VISUAL AND X-RAY DIFFRACTION METHODS

Resonator	Aging Behavior*	Visual Inspection	X-ray Diffraction Inspection
10 Mc Units Failing Acceptance Requirements of $<4x10^{-7}$ During First 30 days			
A-2	Failed 1st mode		extensive banding; surface flaws; clip strain
A-5	Failed 3rd mode	scratch; powder; visible; defect near bottom	defects; scratches; clip strain
A-8	Spurious responses	many shallow scratches	many scratches and flaws; clip strain and oscillation at tab
C-4	Spurious responses	several small scratches in quartz	good; halo on oscillation
C-5	Failed 3rd mode	deep scratch, possible crack, near one clip	center defects; mounting strain; plating boundary
C-7	Spurious responses	many shallow scratches	scratches
D-2	Failed 1st & 3rd	plating buckled near one bond; small scratch-es and large one	bands; plating boundary; clip strain
D-3	Failed in sealing	No Data	No Data
D-4	Failed 3rd mode	plating buckled near bond; small scratches	defect line; plating boundary; clip strain; halo
D-5	Failed-never installed	No Data	No Data
D-6	Failed 1st	plating buckled; scratches; edging poor	few lattice defects; clip strain

*Aging Behavior: high, medium, low refers to the degree of aging, 0 to 4×10^{-7} during first month.

(Continued)

TABLE 3 (Continued)

Resonator	Aging Behavior	Visual Inspection	X-ray Diffraction Inspection
D-8	Failed	plating buckled near bond	bands; clip strain
D-9	Failed 1st	plating buckled near bond; scratches in quartz	twinned one clip; deep scratch or flaw
D-10	Failed 3rd	plating buckled near bond; wafer cracked, possibly on removal	internal bands; wafer cracked on removal
D-11	Failed	plating slightly buckled; shallow scratches	twisted; many small defects; distorted oscillation zone
		10 Mc Units Passing Acceptance Requirements	
A-1	high	edges chipped; scratches; good bond	many small defects or scratches; clip strain; oscillation follows tab
A-3	medium	good bond; many scratches near edge; chipped edge	many defect clusters; scratches; oscillation follows tab
A-4	medium	good bond; chipped edge; scratches; deep scratches in tab	No data
A-6	medium	good bond; chipped edge; scratches; powder spots	No data
A-7	high	good bond; chipped edge; scratched	small scratches and defects; clip strain; oscillation follows tabs
A-9	low	good bond; edge chips; powder spots; small scratches	No Data
A-10	medium	good bond; edge scratches and chips; powder traces	No Data

(Continued)

TABLE 3 (Continued)

Resonator	Aging Behavior	Visual Inspection	X-ray Diffraction Inspection
B-1	medium	good bond; edge chips and scratches; three long shallow scratches	No Data
B-2	low	good bond; edge chips and scratches; other larger scratches	few line defects and scratches; clip strain; oscillation follows tabs
B-3	medium	good bond; edge scratch-es and chips; other scratches	No Data
B-4	low	good bond; edge chips; small scratches over face	No Data
B-5	medium	good bond; edge scratches and chips; other scratches	clean pattern; clip strain; edge strain oscillation follows tabs
B-6	high	bonding fair; large edge chips; scratches; plating scratched and pealed	defect clusters; clip strain; oscillation follows tabs
B-7	low	bonding fair; edge chips; scratches edge and face; powder spots	No Data
B-8	medium	good bond; edge chips; surface scratches	No Data
B-9	high	bonding fair; edge badly chipped; scratches over face; plating scratched at tab	No Data
B-10	low	good bond; edge chips	No Data
C-1	medium	bond good; edge chipped; scratches	band and line defects; small clusters
C-2	medium	bond good; edge chipped; scratched badly	No Data

(Continued)

TABLE 3 (Concluded)

Resonator	Aging Behavior	Visual Inspection	X-ray Diffraction Inspection
C-3	high	bond good; numerous edge chips and scratches	edge grinding strain; clip strain otherwise clean
C-6	low	bond good; small scratches and one severe one	band; especially one edge some clusters
C-9	high initially	bond good; edge chipped; face and plating scratched	No Data
C-10	medium	erratic after 330 days	band structures through center zone; clip strain
C-11	medium	erratic at 365 days	defect band and zone; clip strain; non-uniform oscillation zone intensity
C-12	medium	bond good, edge chipped; surface scratched	No Data
D-7	medium	bond good, edge chipped; small scratches	No Data
D-12	low	plating pealed near tabs; edge chipping; small scratches	No Data

defects and strain associated with a large portion of both the poor and good units. Particular examples such as A-2, A-5, D-2, D-11 and others were removed from their containers, etched in ammonium bifluoride solution (saturated at room temperature) for periods of about 2.5 hours to 4 hours and refabricated in the cement study series. Even though A-2 possessed one of the most intense internal banding patterns observed in any x-ray topographs, it performed very stably indeed after refabrication. It therefore appears that in at least four examples for AT-Cut resonators, surface defects or mounting arrangements were of much greater importance in degrading aging than were internal defects of the nature occurring in these units.

Of particular interest to the behavior of the units were results obtained subsequently and reported under section IV C 5 covering bonding cements. The oscillatory zone of a crystal may follow the plating tabs to the mounting clip as is shown in Figure 11. A combination of surface defects, bonding cement, and possibly scratches in the plating may affect both drive sensitivity and aging. The effect of surface scratches has been reported by Smagin.[11]

Another factor, not previously discussed, is that if appreciable acoustic energy be transferred to the spring clip or tab mount via the plating tab oscillating zone, the possibility exists that strain anneal or fatigue in the metal support will affect aging; and, indeed, is likely. There is agreement here also with respect to the aging mechanism of low frequency resonators as suggested by Byrne et. al.[7] The mount is stated by Byrne to play a significant part in high positive aging vectors of low frequency resonators.

In conclusion, the x-ray studies have pointed to many interesting types of behavior in the 10 Mc resonators that must certainly be associated with aging. However, prediction of aging of 10 Mc units from the x-ray diffraction

[11] A. G. Smagin, "Methods of Reducing the Energy Dissipated in the Surface Layers of Quartz," Krystallografiya 4, No. 6, pp 862-866, November-December 1959 (English translation)

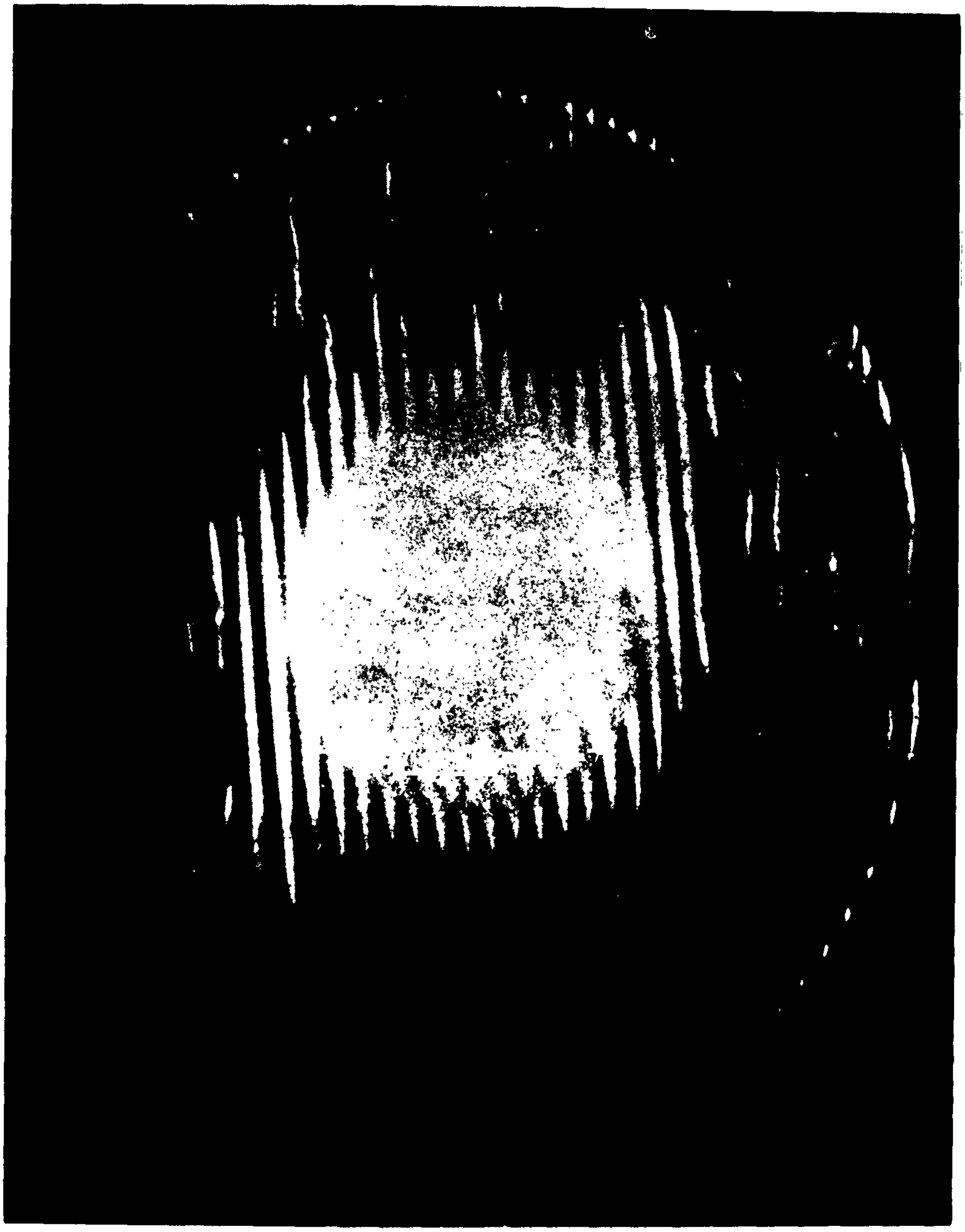

Figure 11. X-ray SID diffraction pattern of 10 Mc resonator A-1 while oscillating. Note oscillation following path of plating tabs.

pattern exhibit of defects alone is not feasible at this stage of our study. In resonators of other frequencies and for certain specific zone defects correlation has proved to be better.

5. Aging of 10 Mc Resonators Bonded with Various Cements

The aging of groups of 10 Mc AT-Cut resonators bonded respectively with one of the five selected cements, du Pont 5504, du Pont 5605, Bondmaster,* Bakelite,* and Pyroceram,* has been summarized in some detail in Quarterly Reports Nos. 6 and 7. In short, some 68 resonators approximately equally divided among the various cements were fabricated. In the initial stages, begun in May 1964, units bonded with Bakelite-silver and Pyroceram-silver performed so poorly that methods of improvement in fabrication were sought. As a result of this, the quartz plates of the latter two groups were etched approximately 2.5 hours in ammonium bifluoride solution saturated at room temperature. In addition a jig was made for exact bending and alignment of the mounting clips, a narrower tab was plated, and the cement was applied to the quartz on the plated tab side only. These latter improvements brought these units into a satisfactory performance range. Five units bonded with du Pont 5504 cement were similarly prepared.

Aging of these units was continued for 55 to 190 days, dependent on the order of fabrication. They were then removed from the aging oven and placed for five minutes in a muffle furnace maintained at a temperature of 300°C. For exposure the units were seated upright in cavities in a small fire brick which extended just above the base pins and seal. The body of the container and the crystal plate were fully exposed to radiation from the walls of the furnace. The temperature which the crystal attained was not determined although it appears doubtful that it reached 300°C during the five minute period.

* Binder only. Silver flake is added to form a conductive cement. Bondmaster was type M-640 and the Pyroceram No. 95.

The aging distribution for the variously bonded units observed before exposure to the 300°C heat cycle is displayed in the bar graphs of Figure 12 and in Table 4. From the table it will be noted that almost all units passed the initial specification of $< 4 \times 10^{-7}$ change in frequency during the first four weeks. By applying the more drastic standards of the bar graph, $< 1 \times 10^{-7}$ during the first 30 days it is observed that the du Pont 5504, du Pont 5605 and Bondmaster gave the more stable units in that order and a higher yield based on $< 2 \times 10^{-7}$ for the total period. However, all units gave reasonably good performance and especially with respect to aging rate during the final 30 day aging before 300°C cycling.

The results of cycling to 300°C are shown in Table 5 for all units examined and are summarized at the bottom of the table and in a different form below.

Cement	Total Units	No Units Changing in Frequency $\leq \pm 5 \times 10^{-7}$	Percentage of Total
5504(not etched)	8	0	0
5504(etched)	5	4	80
5605(not etched)	13	5	38.4
Bondmaster(not etched)	11(2 discarded)	8	72.5
Bakelite(etched)	16	6	37.5
Pyroceram(etched)	13	5	38.5

On the other hand some units shifted by very large amounts, the maximum observed being -97.5×10^{-7} for a 5504 bonded unit plated in the early series. The possibility that this unit is a leaker exists.

Aging data of an exceptionally good unit of each type are displayed in Figures 13 to 17. Aging performance subsequent to the 300°C temperature cycle was predictable only to the extent that a recovery period at a fairly sharp slope usually occurred during the first 30 days. The aging of the

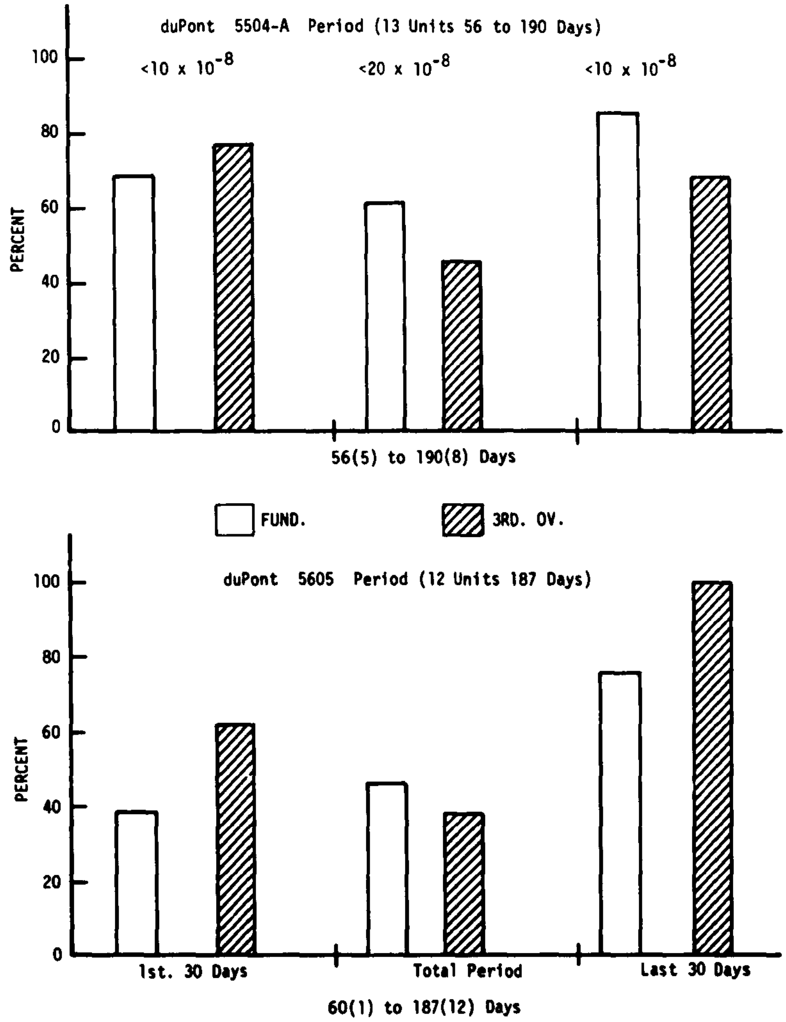

Figure 12. Aging performance distribution of 10 Mc resonators bonded with various cements.

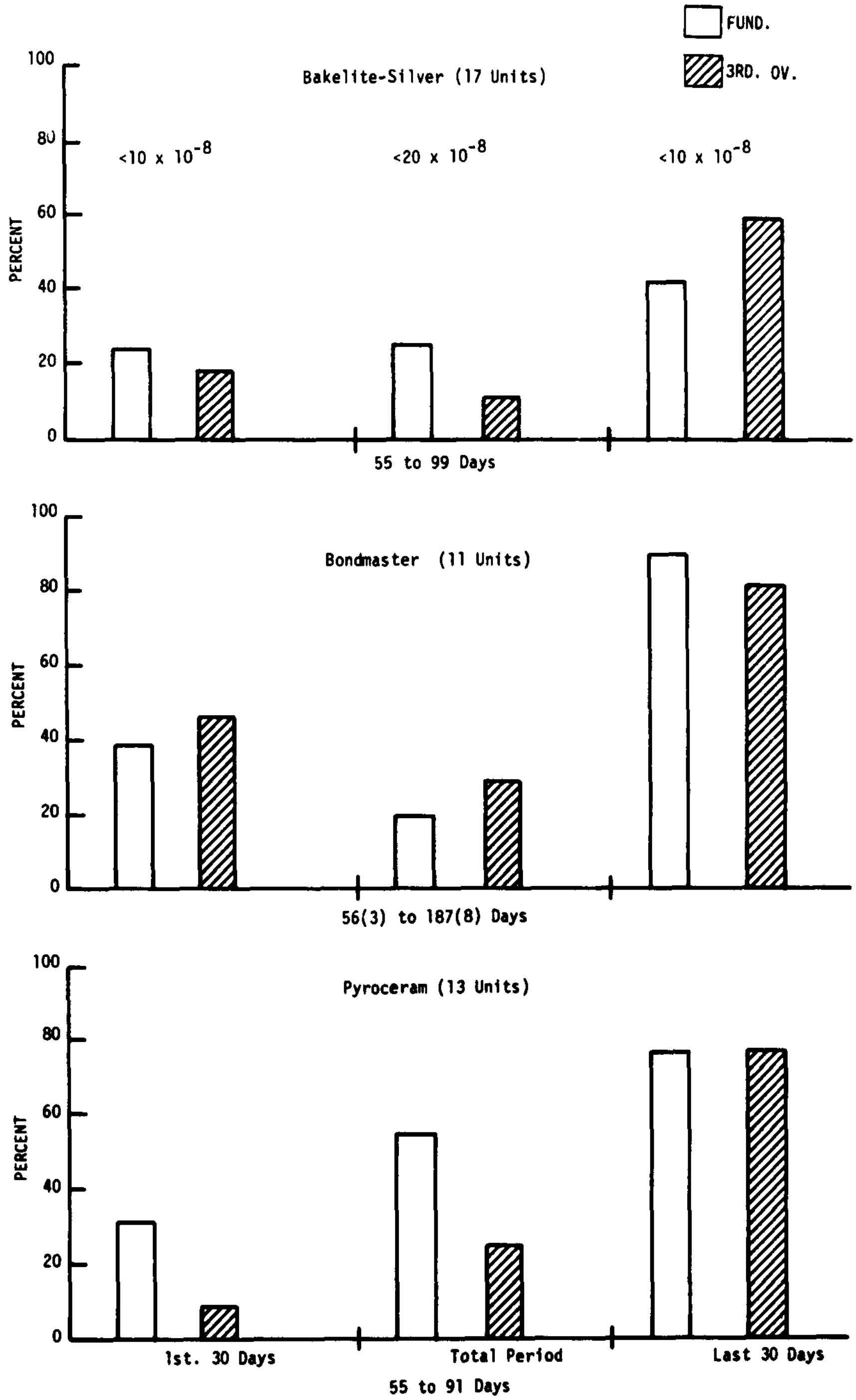

Figure 12 (Continued). Aging performance distribution of 10 Mc resonators bonded with various cements.

TABLE 4

AGING PERFORMANCE OF 10 MC
RESONATORS IN BONDING MATERIAL EVALUATION

	No. of resonators	No. passing $<4x10^{-7}$/1st 30 days 1st mode	3rd mode	No. passing $<4x10^{-7}$/each 30 days 1st mode	3rd mode	Comments
duPont 5504-A	13	13	13	13	13	1 border-line case
duPont 5605	13	13	13	12	13	1 unit failed fundamental after 4 mos.
Bakelite-silver	17	11	13	14	15	these units were etched 30' to 150'. The units etched 30' exhibited high positive slopes initially. The units etched 150' aged at lower rates.
Bondmaster-silver	13	11	11	11	11	two units poor-not plotted one scratched one high R_s (poor oven position)
Pyroceram	13	11	13	12	13	
Totals	69	59	63	62	65	

TABLE 5

FREQUENCY CHANGES OBSERVED AFTER EXPOSURE OF 10 MC RESONATORS TO TEMPERATURE OF 300°C FOR 5 MINUTES

Unit	Date Aging Started	Etch Time (Hours)	Plating Mask	Bonding Cement	ΔF(pp10^7) Fund.	ΔF(pp10^7) Third	ΔR_s(ohms) Fund.	ΔR_s(ohms) Third	Remarks
E-1	5-19-64	16.0	narrow tab	5504	-25.2	-	+1.0	-	
E-2	"	16.0	"	"	- 9.4	-	n.c.	-	
E-3	"	none	"	"	-15.1	-14.5	+0.5	+1.0	
E-(C-5)	"	17.5	"	"	- 4.2	-	-2.5	-	Pierce osc. drive 6-15-64
E-(D-2)	"	8.5	"	"	-11.5	-18.9	-2.5	-7.0	bad oven pos.
E-(D-4)	"	16.0	"	"	+ 7.5	-	+0.5	-	Pierce osc. drive 6-26-64
E-(D-6)	"	18.0	"	"	+ 2.7	-	n.c.	-	Pierce osc. drive 6-26-64
F-(A-2)	"	2.0	"	"	-28.8	-24.5	+0.5	n.c.	v.g. unit
F-(A-5)	"	2.0	"	"	- 7.9	- 7.9	+0.5	+0.5	v.g. unit
F-(D-11)	"	4.0	"	"	-57.4	-48.6	+0.5	+1.0	
5504-2	5-19-64	0.5	wide tab	5504	-56.5	-36.6	+1.0	-2.5	possibly bad oven position
5504-3	"	0.5	"	"	-93.5	-67.5	+2.0	+9.5	erratic after heating
5504-5	"	0.5	"	"	+27.1	+25.8	+0.5	n.c.	
5504-7	"	0.5	"	"	+48.1	-52.0	+3.5	-1.5	unusual results
5504-8	"	0.5	"	"	+19.0	+16.0	+0.5	+1.0	
5504-9	"	0.5	"	"	+ 7.3	+20.8	+3.5	+2.0	poor after heating
5504-10	"	0.5	"	"	+39.5	+26.3	n.c.	+1.5	prob. bad oven position
5504-12	"				+23.5	+24.7	-0.5	n.c.	
5504-A	5-25-64	2.5	narrow tab	5504	+11.3	+ 5.5	+1.0	+0.5	
5504-B	"	2.5	"	"	+ 1.4	- 0.03	-1.0	-1.0	
5504-C	"	2.5	"	"	+ 1.6	+ 1.8	n.c.	n.c.	
5504-D	"	2.5	"	"	- 2.1	- 2.5	n.c.	+0.5	
5504-E	"	2.5	"	"	- 3.7	- 3.9	-0.5	n.c.	
5605-1	5-19-64	0.5	wide tab	5605	+ 0.6	- 1.0	-1.0	-1.0	
5605-2	"	0.5	"	"	- 9.1	- 6.0	+1.0	+1.0	
5605-3	"	0.5	"	"	-28.1	- 9.6	-2.5	+2.5	
5605-4	"	0.5	"	"	-30.3	-12.2	n.c.	+1.0	poor unit
5605-5	"	0.5	"	"	- 4.3	+ 7.0	+2.0	+0.5	bad oven pos.
5605-6	"	0.5	"	"	- 1.3	+ 3.3	n.c.	+3.0	
5605-7	"	0.5	"	"	- 2.0	-11.2	+2.0	+0.5	

(Continued)

TABLE 5 (Continued)

Unit	Date Aging Started	Etch Time (Hours)	Plating Mask	Bonding Cement	ΔF($pp10^7$) Fund.	ΔF($pp10^7$) Third	ΔR_s(ohms) Fund.	ΔR_s(ohms) Third	Remarks
5605-9	5-19-64	0.5	wide tab	5605	-14.3	- 7.1	n.c.	+ 2.5	poor on fund. ΔF questionable
5605-10	"	0.5	"	"	- 3.9	- 4.2	n.c.	+ 0.5	
5605-11	"	0.5	"	"	+ 3.3	- 5.5	+0.5	+ 1.5	
5605-12	"	0.5	"	"	+ 6.4	- 9.3	-0.5	+13.0	poor on third
5605-13	"	0.5	"	"	-10.2	- 4.1	+3.5	- 0.5	
5605-14	"	0.5	"	"	+14.3	+ 1.9	+1.0	n.c.	
BM-1	5-19-64	0.5	wide tab	Bondmaster Silver	+ 4.4	-14.3	-0.5	- 2.0	poor on third
BM-2	"	0.5	"	"	- 0.1	+ 4.7	n.c.	+ 0.5	
BM-3	"	0.5	"	"	- 0.1	+ 2.4	n.c.	+ 1.5	
BM-6	"	0.5	"	"	+ 9.6	+ 9.8	-0.5	- 0.5	
BM-8	"	0.5	"	"	- 8.2	+ 2.4	n.c.	+ 0.5	
BM-9	"	0.5	"	"	- 1.0	- 0.4	n.c.	n.c.	
BM-10	"	0.5	"	"	+10.0	- 1.1	n.c.	+ 2.0	
BM-11	"	0.5	"	"	+15.5	- 2.9	n.c.	- 2.5	
BM-A	9-25-64	2.5	narrow tab	Bondmaster Silver	-24.3	-12.0	+2.0	+ 5.0	may be leaking
BM-B	"	2.5	"	"	+ 1.4	+ 2.7	+1.5	+ 1.5	
BM-C	"	2.5	"	"	- 0.9	- 0.7	-0.5	- 0.5	
BM-D	"	2.5	"	"	- 0.3	- 2.5	-0.5	n.c.	ΔF taken from 11-20-64 measurement
BM-E	"	2.5	"	"	- 1.0	+ 0.5	-1.5	+ 0.5	poor unit and/ or bad oven position
BK-C	8-14-64	0.5	narrow tab	Bakelite Silver	+ 4.4	+ 8.8	+0.5	+ 1.0	
BK-E	"	0.5	"	"	-48.1	-33.4	+4.0	+ 0.5	
BK-H	"	0.5	"	"	-41.4	-42.8	+1.0	+ 1.5	
BK-I	"	0.5	"	"	-30.4	-20.9	+0.5	+ 5.5	
BK-J	9-8-64	2.5	"	"	+ 4.0	+ 3.0	+0.5	n.c.	
BK-K	"	2.5	"	"	- 8.5	- 6.5	+1.0	+ 1.0	
BK-L	"	2.5	"	"	- 0.8	- 1.1	+1.0	+ 0.5	
BK-N	"	2.5	"	"	+ 5.0	+ 7.7	n.c.	n.c.	
BK-O	"	2.5	"	"	+ 9.0	+ 8.3	-0.5	+ 0.5	fund. poor. ΔF of questionable value.

(Continued)

TABLE 5 (Continued)

Unit	Date Aging Started	Etch Time (Hours	Plating Mask	Bonding Cement	ΔF(pp10^7) Fund.	ΔF(pp10^7) Third	ΔR_s(ohms) Fund.	ΔR_s(ohms) Third	Remarks
BK-P	9-8-64	2.5	narrow tab	Bakelite Silver	+ 0.9	+ 3.3	+0.5	+ 1.0	
BK-Q	"	2.5	"	"	- 6.9	+ 2.2	n.c.	+ 0.5	
BK-R	"	2.5	"	"	- 0.9	+ 4.0	+1.0	+ 0.5	
BK-S	"	2.5	"	"	- 4.4	- 5.5	+0.5	+ 1.5	
BK-T	10-6-64	2.5	"	"	+13.8	+14.5	+1.0	+ 0.5	
BK-U	"	2.5	"	"	+ 6.4	+ 7.0	n.c.	n.c.	
BK-V	"	2.5	"	"	+ 7.9	+ 9.2	n.c.	n.c.	
PY-D	8-22-64	0.5	narrow tab	Pyroceram Silver	+12.5	+21.4	n.c.	+ 0.5	poor on third
PY-G	"	0.5	"	"	+15.3	+14.5	n.c.	+ 0.5	
PY-K	9-21-64	2.5	"	"	+ 9.1	+12.6	n.c.	n.c.	
PY-L	"	2.5	"	"	+ 4.8	+ 4.3	+0.5	n.c.	
PY-M	"	2.5	"	"	+26.7	+ 5.6	+3.0	n.c.	poor on fund.
PY-N	"	2.5	"	"	+ 7.5	+ 3.2	n.c.	n.c.	
PY-O	"	2.5	"	"	+ 2.4	+ 2.4	n.c.	n.c.	
PY-P	"	2.5	"	"	+13.5	+15.0	n.c.	n.c.	
PY-Q	"	2.5	"	"	+ 6.8	+ 8.1	n.c.	n.c.	
PY-R	10-6-64	2.5	"	"	+ 4.7	+ 6.4	n.c.	+ 1.0	
PY-T	"	2.5	"	"	+10.2	+10.4	n.c.	n.c.	
PY-U	"	2.5	"	"	- 0.9	+ 3.8	n.c.	n.c.	poor unit
PY-V	"	2.5	"	"	+ 3.2	+ 2.4	n.c.	n.c.	poor unit

Average Values

Cement	ΔF(pp10^7) Fund.	ΔF(pp10^7) Third	ΔR_s(ohms) Fund.	ΔR_s(ohms) Third	Remarks
5504*	21.9	24.7			5 letter series units held up very well
5605	9.85	6.4			
Bondmaster Silver	6.05	4.33			Best group
Bakelite Silver	+12.05	11.12			
Pyroceram Silver	9.03	8.43			Probably most uniform group

* Includes group E and F.

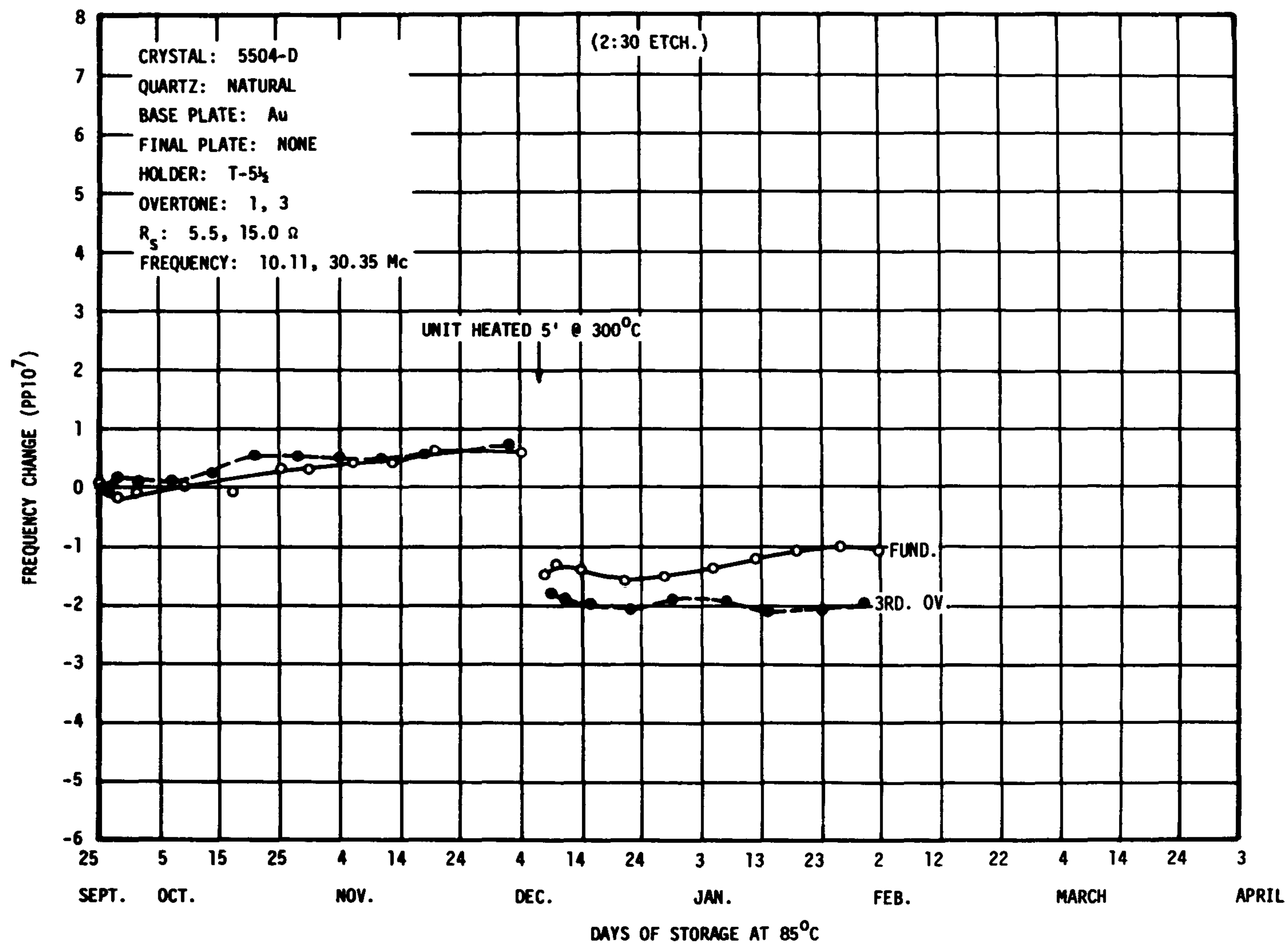

Figure 13. Aging data for 10 Mc resonator 5504-D, cement study series.

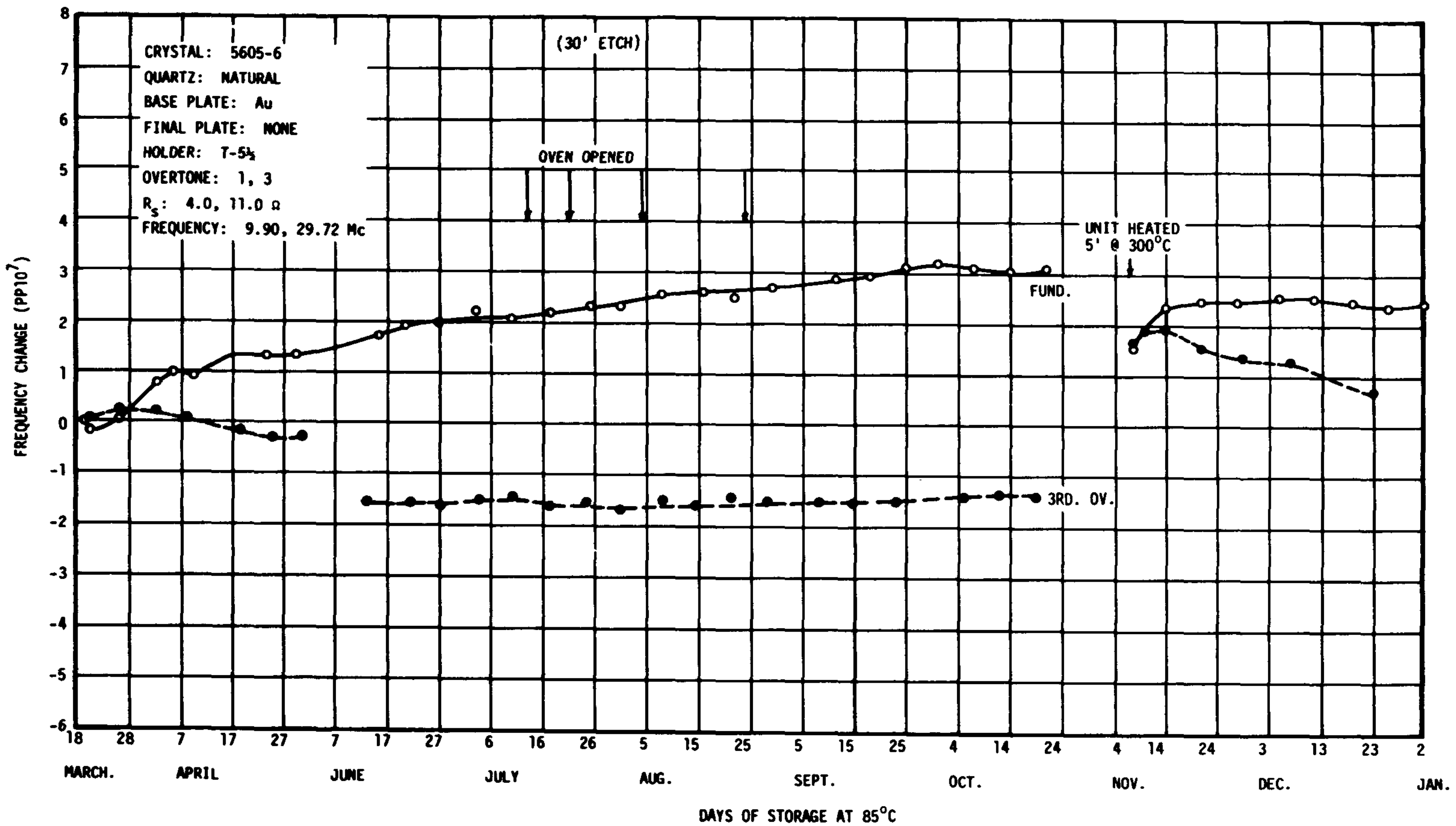

Figure 14. Aging data for 10 Mc resonator 5605-6, cement study series.

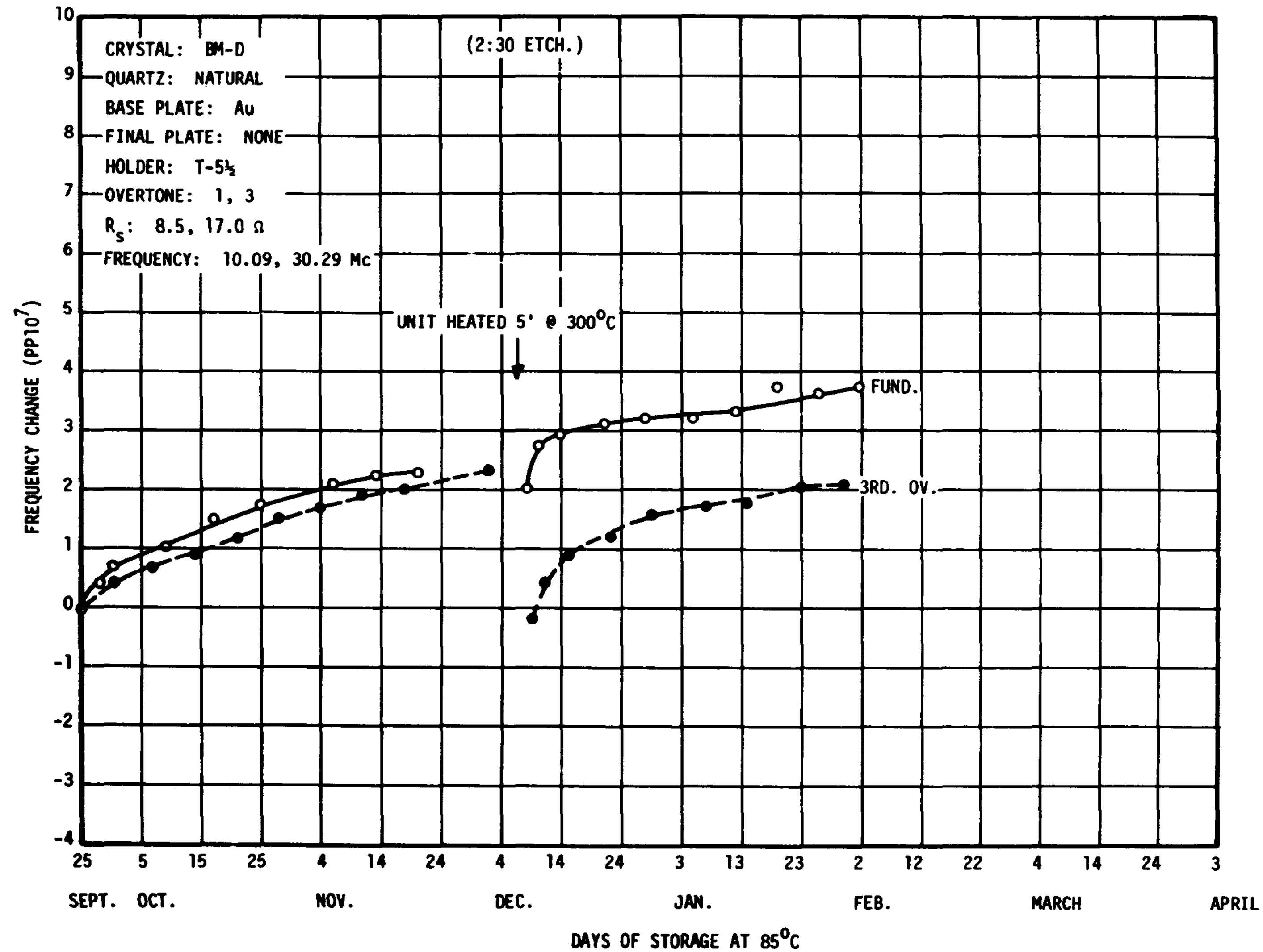

Figure 15. Aging data for 10 Mc resonator BM-D, cement study series.

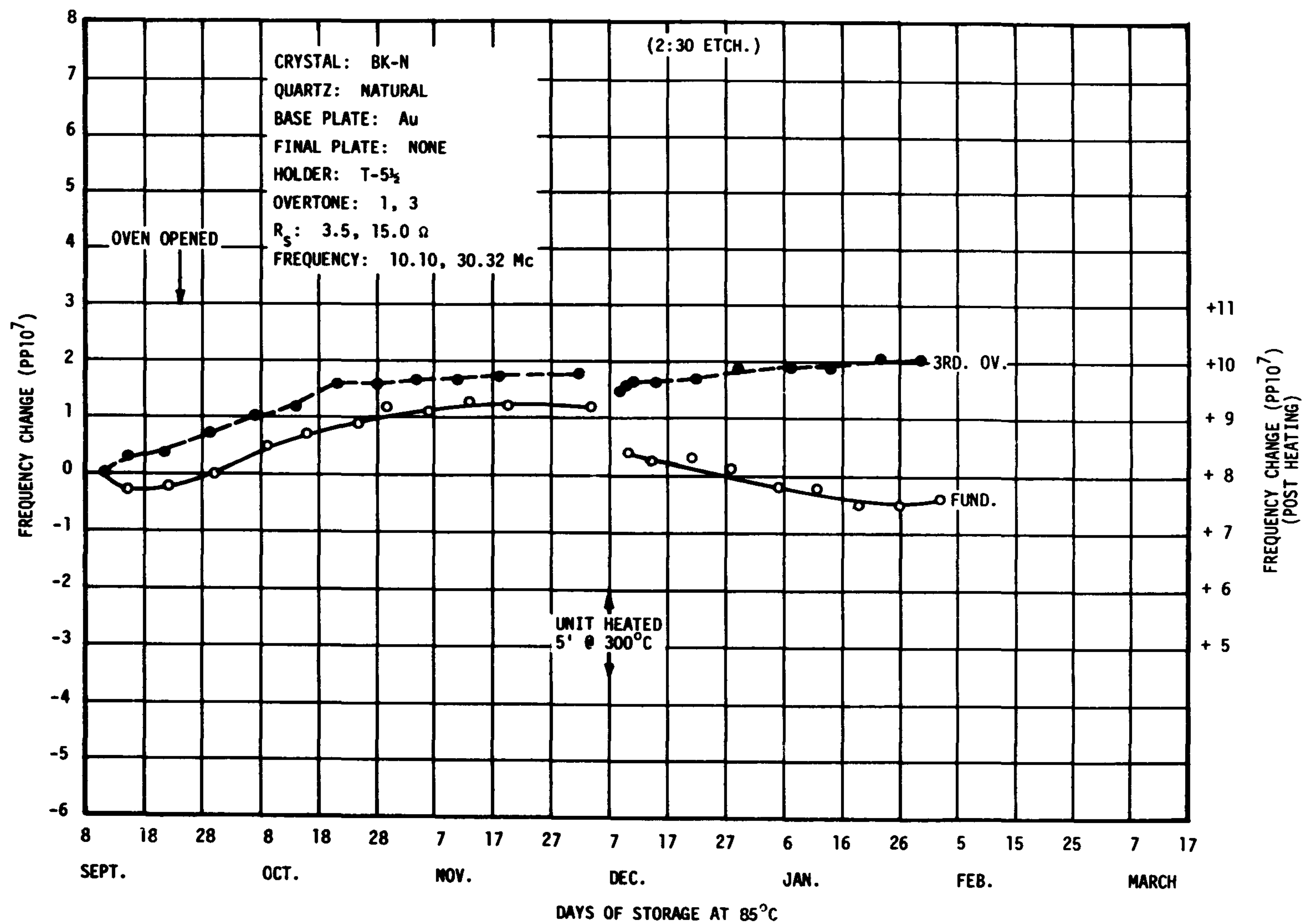

Figure 16. Aging data for 10 Mc resonator BK-N, cement study series.—

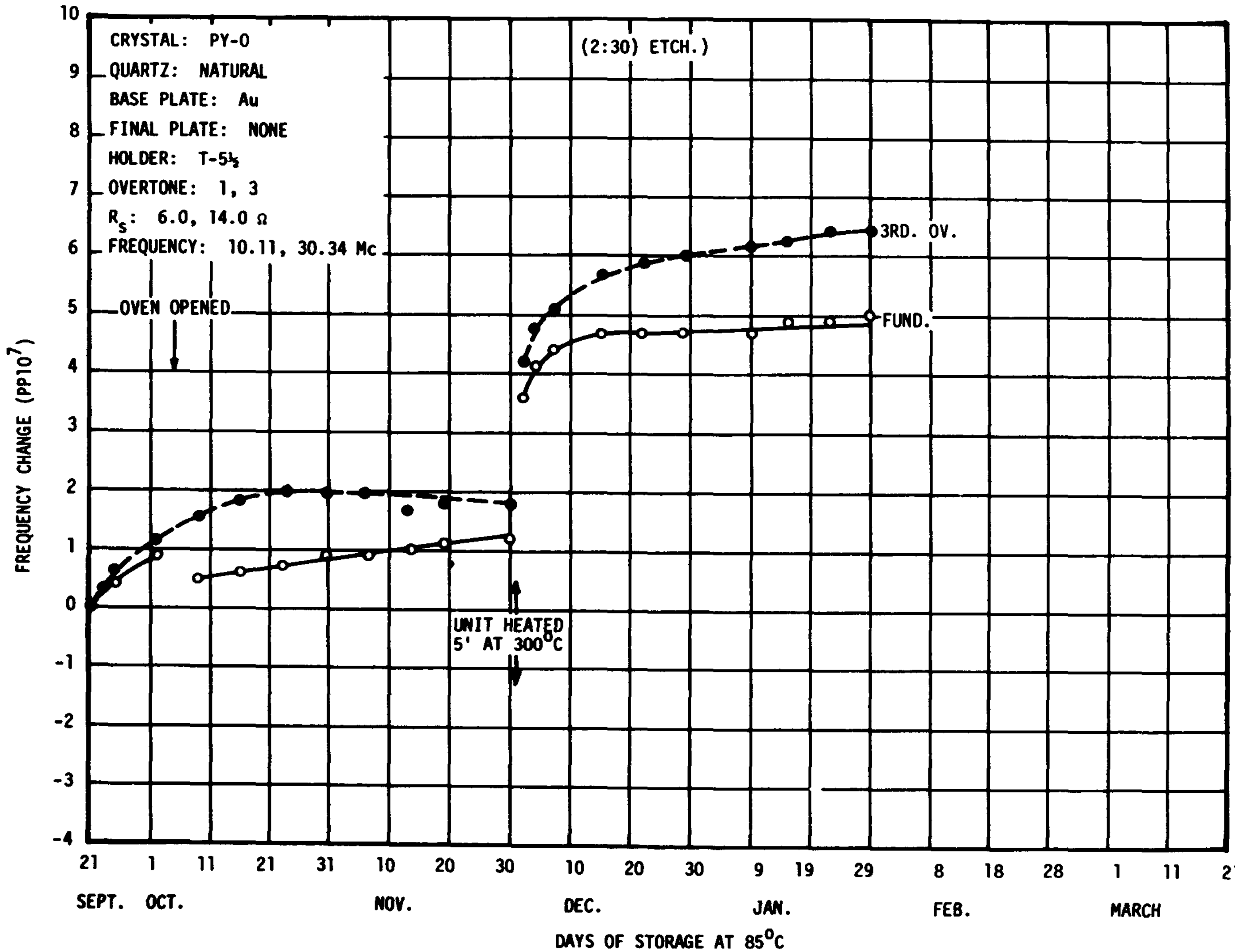

Figure 17. Aging data for 10 Mc resonator Py-O, cement study series.

better units then returned close to the original rate and direction. However, there were many units exhibiting erratic behavior.

The general improvement in aging performance as a result of etching resonators before bonding with Bakelite or Pyroceram has already been discussed. Here we see evidence that resonators bonded with du Pont 5504 are upgraded by etching also. It appears quite probable that all resonators of the type under discussion will benefit from the etch step before plating where critical frequency stabilities are involved. This etch step has been instituted by us for use in all further resonator fabrication conducted here.

Judging from overall performance and based on the temperature cycle described it appears that Bondmaster may be the best cement. If the etch technique is employed it is probable that 5504, 5605 and Bondmaster will be nearly comparable for etched units. Pyroceram bonded units were noteworthy because of high uniformity in direction and magnitude of changes in frequency experienced whereas other units were more random in degree and direction of change. Bakelite, after etching, performed reasonably well. In general, subsequent aging changes are relatively small for all resonators exhibiting small change due to temperature cycling as may be observed in Figures 13 thru 17.

6. Relation of Drive Sensitivity to Aging of 10 and 16 Mc Resonators

In Quarterly Report No. 6 an account of the apparent relation of drive sensitivity to aging was given, and this was further summarized in Quarterly Report No. 7. The latter account, being a summary, is repeated in this Interim Report.

The fact that certain units were drive sensitive and others were not has been noted over a period of several years. However, a relation between this effect and aging or to any other consistent fabrication parameter had not been established prior to the current research work. Under the latter it was first noted that the aluminum coated 16 Mc resonators prepared for the pulsed radiation exposure were considerably more stable on the average than the other units. Subsequently in the 10 Mc reliability series and in the cement studies, particularly the latter, more careful examination of possible variables such as density of plating, width of the tab, type of cement and x-ray diffraction information with regard to strain and defects were considered. It became evident that greater variability was observed for resonators bonded with specific cements, namely Bakelite-silver and Pyroceram-silver.

An effort to analyze the peculiar behavior of units such as A-2 (see Quarterly Report No. 5, Figure 7) of the reliability series, which had a tremendous variety of defect detail in its x-ray diffraction SID pattern, lead to etching for removal of surface defects in order to separate the possible effect of these from those of internal defects. The improvement of the aging of the resonator after etching and remounting (Figure 3, Quarterly Report No. 6) was astonishing. It then became apparent that surface etching was removing both drive sensitivity and poor aging behavior. Choice of cement enhanced or diminished the effect, and an explanation for the apparent poor results for Bakelite-silver and Pyroceram bonding agents is that they tended to enhance drive sensitivity caused by surface or other defects that were already present. Results from etching a large number of units now

indicate that etching removes many of the defects, but scratches in the plating or inaccessible internal faults still result in a poorer percentage of very stable units with the more rigid cements.

A number of drive level measurements have now been obtained for several units with good and bad aging. An example of the stability of the R_s and the frequency of a resonator of good aging performance with respect to changes in drive level is shown in Figure 18. The usual drive is about 6 microwatts but here we have varied the drive over the approximate range 1 to 100 μW. It will be noted that for this unit, BK-V, virtually no change in frequency or R_s was observed. The aging data for the unit are shown in Figure 19. Its frequency has changed only about +1 part in 10^7 during the first 30 days.

In contrast to the behavior of BK-V, observe that of unit BK-W in Figure 20A. The drive sensitivity data in Figure 20A exhibit a negative shift of the unit of over 10 ppm for the same drive level range of BK-V and the R_s shifts markedly also. The aging of this unit was +8.8 ppm in the first 2 days and was not plotted. The third mode aged poorly also. An x-ray diffraction SID pattern of this unit while oscillating displays in Figure 20B for the normal $(2\bar{1}0)$ reflection a very atypical oscillation pattern of non-uniform intensity and oscillation about bonds. Patterns made with other reflection are also unusual in appearance. A defect zone near one edge is visible. It is probable that the poor behavior of this unit is directly attributable to a poor quartz blank in this case.

An even more interesting detail is brought out in Figure 21. Here the drive sensitivity of a unit at its fundamental and the third overtone

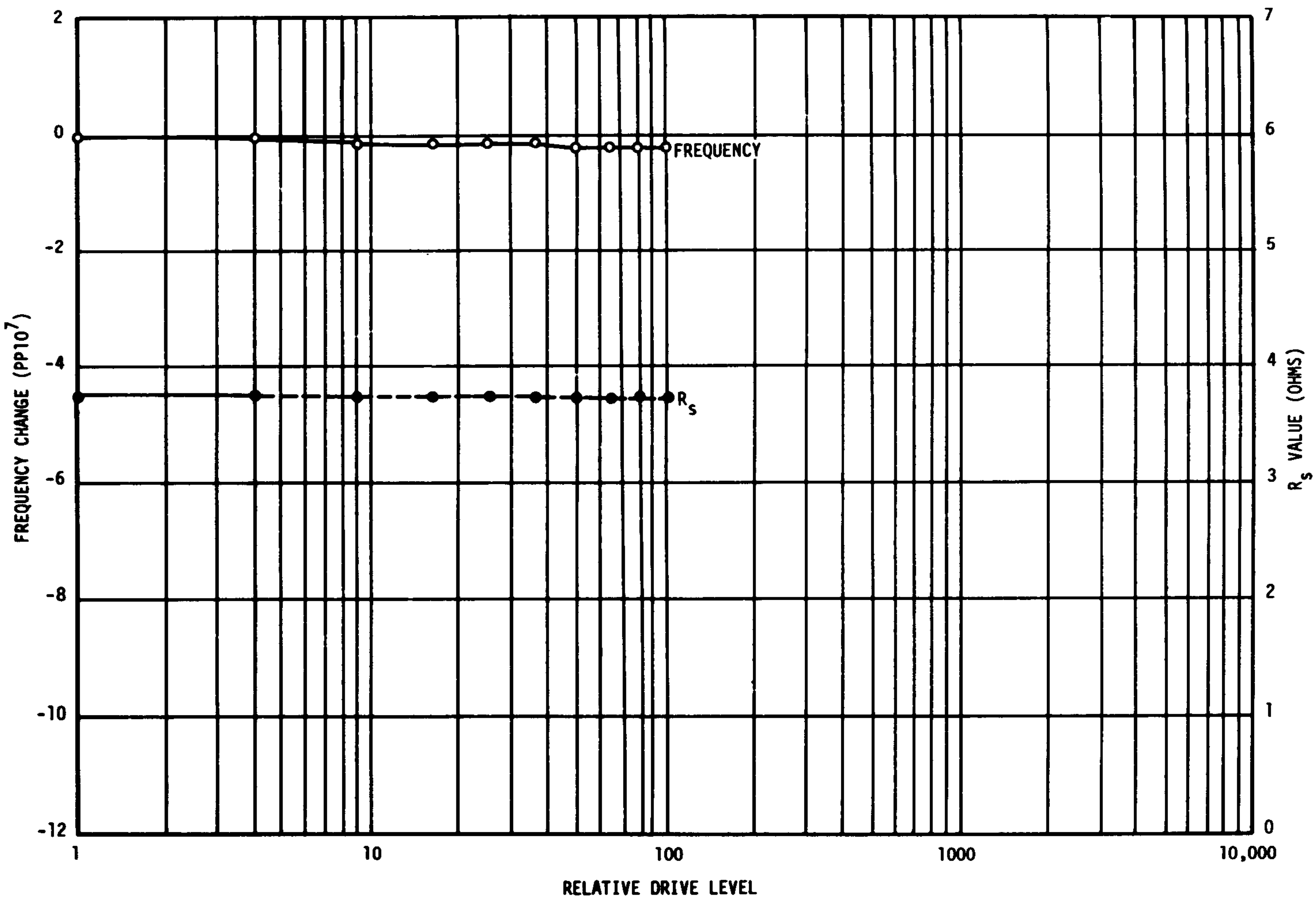

Figure 18. Data on drive sensitivity for 10 Mc resonator BK-V.

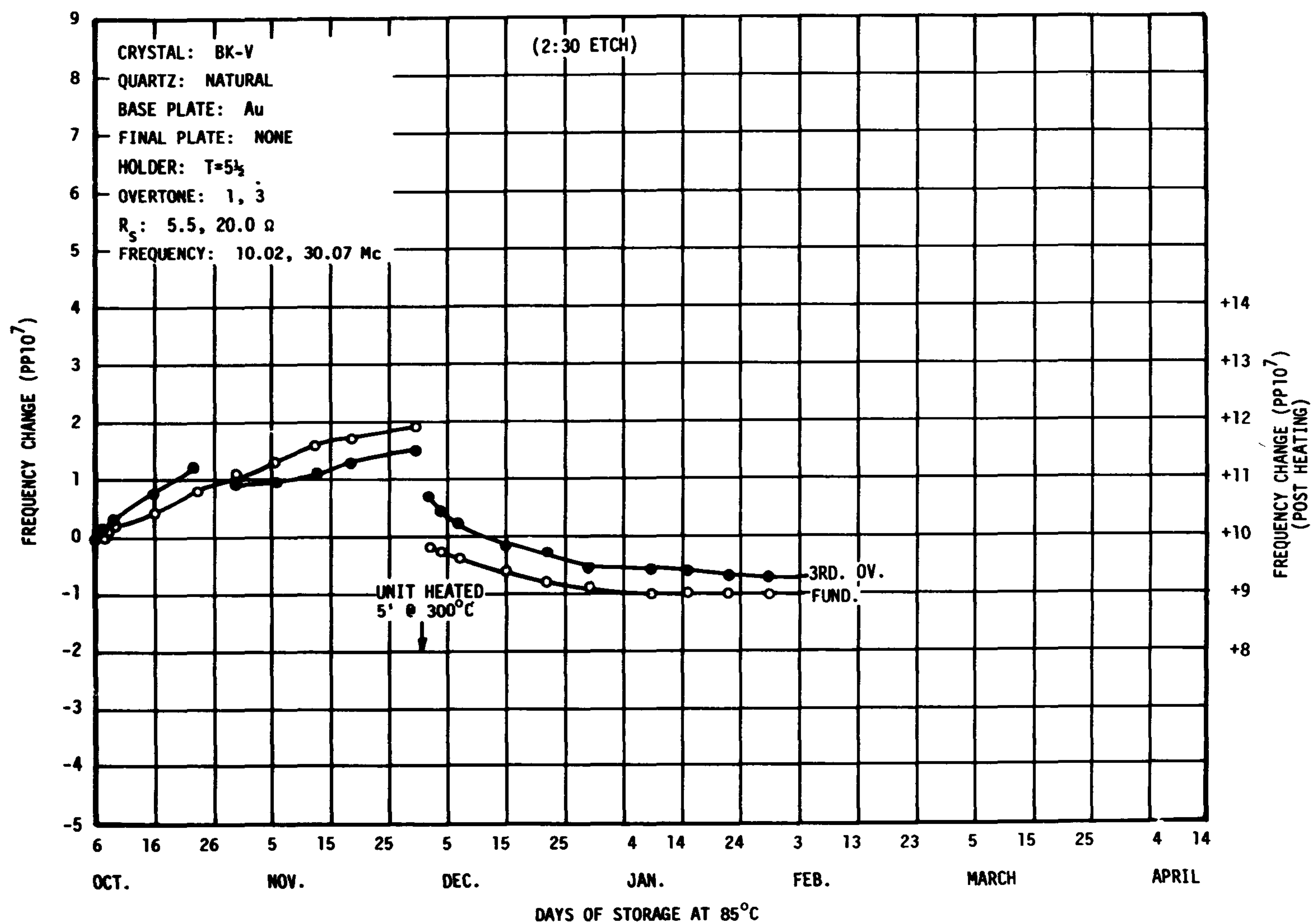

Figure 19. Data on aging of 10 Mc resonator BK-V.

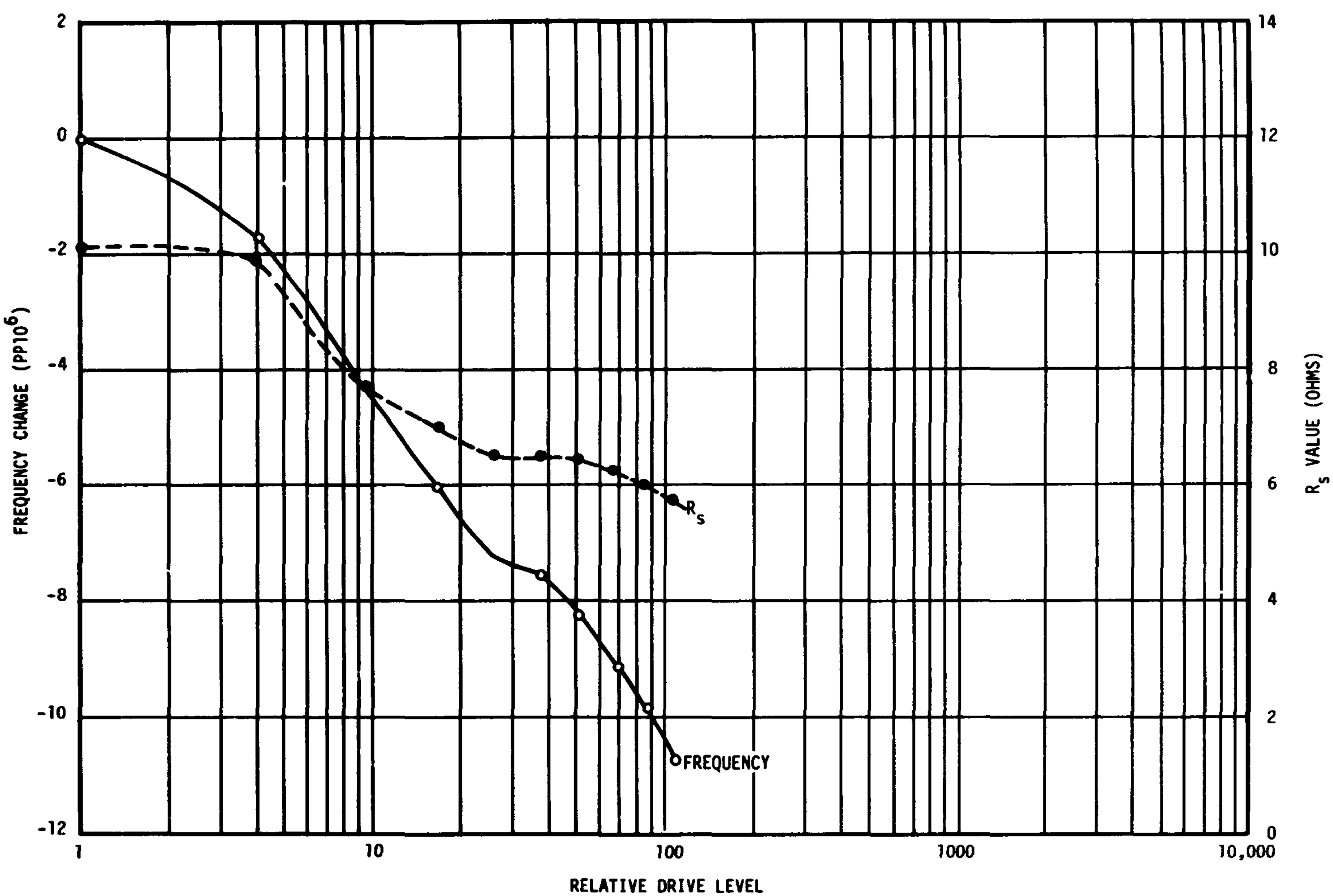

Figure 20a. Data on drive sensitivity of 10 Mc resonator BK-W.

Figure 20b. X-ray SID diffraction pattern of resonator BK-W while oscillating, ($2\bar{1}0$ reflection.) Note atypical oscillation pattern with varying zones of intensity and with oscillating zone about bond.

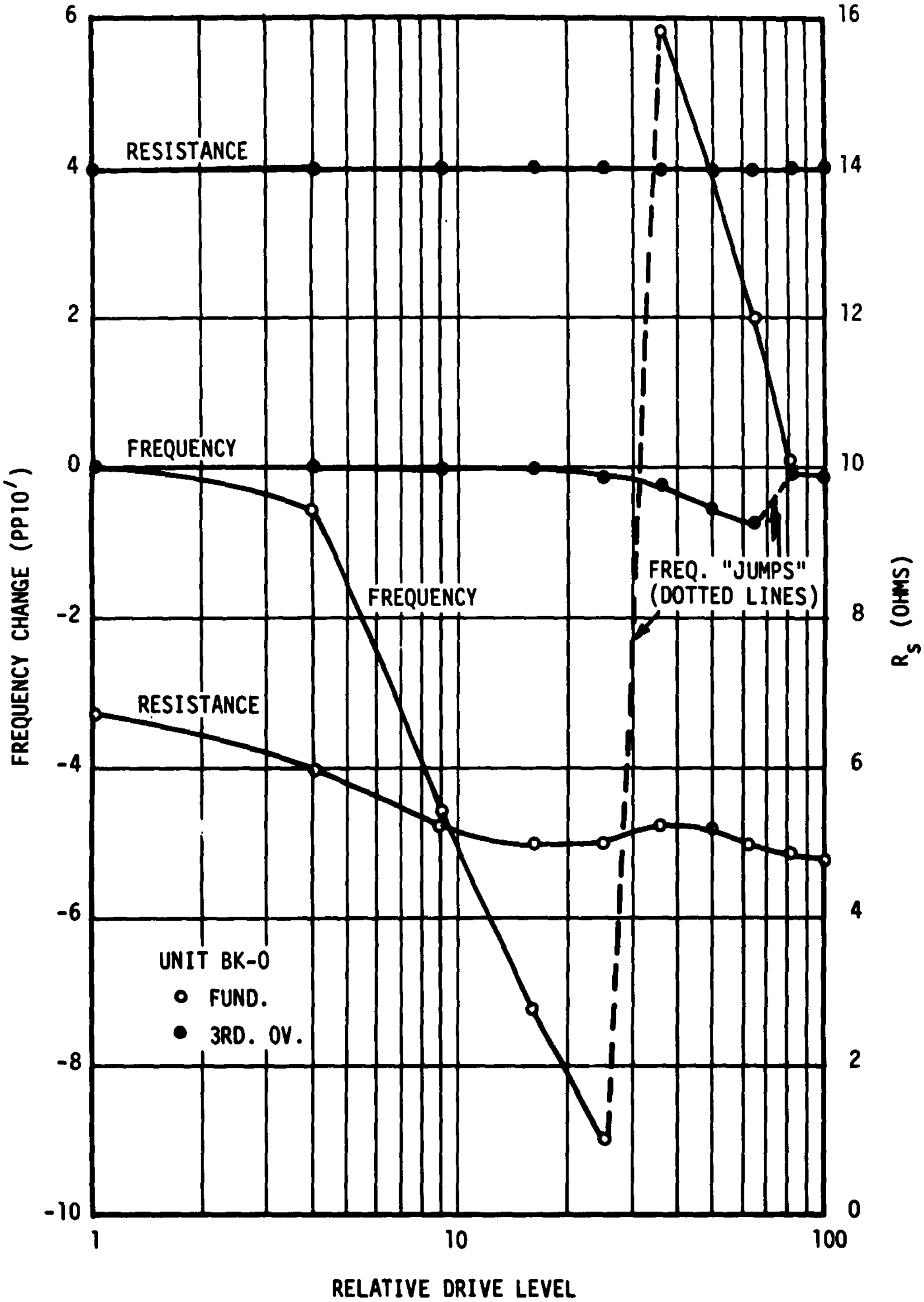

Figure 21. Data on drive sensitivity of 10 Mc resonator BK-O.

are displayed. Whereas the overtone mode was relatively insensitive to drive level changes the fundamental mode was quite sensitive. The aging, as may be expected, was poor at the fundamental and excellent at the overtone as may be seen in Figure 22.

Since the patterns illustrated are typical of many units observed it is apparent that one can predict with reasonable accuracy that a drive sensitive unit will perform poorly in subsequent aging measurements. A better understanding of causes of drive sensitivity would give a better understanding of causes for aging. One possible reason for drive sensitivity is that as the amplitude of drive is increased the region undergoing oscillation increases in volume (and surface area) and penetrates regions of the crystal of differing characteristics. The fundamental mode has both a larger active zone and no "anchor points" in the initial material. In general then, the fundamental mode may be expected to be more drive sensitive than an overtone mode.

7. Summary of Effects of Irradiation on 16 Mc Resonators

The results of experiments on the irradiation of 96 16 Mc AT-Cut resonators was detailed in Quarterly Report No. 4. A graphic summary of the same information is presented in Figure 23. The total expected shift of the frequency of a given variety of quartz given a specific type of treatment can be determined from this graph.

An examination of these data shows that effects due to temperature cycling were sufficient to mask any frequency shift resulting for resonators of natural or swept cultured quartz exposed at SPRF. However, the resonators of the natural quartz did display a negative shift of 5.7 pp 10^7 when

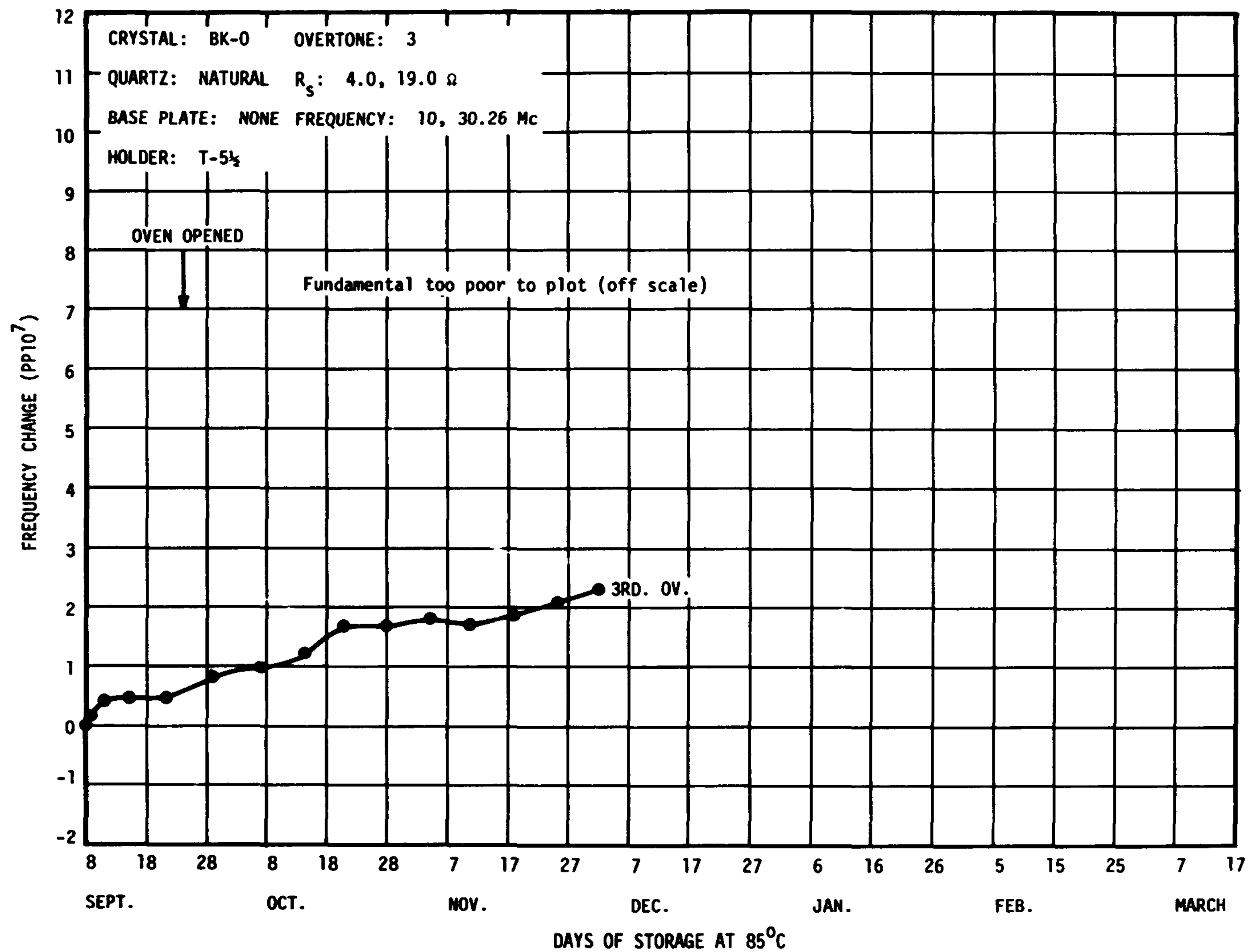

Figure 22. Data on aging of 10 Mc resonator BK-0.

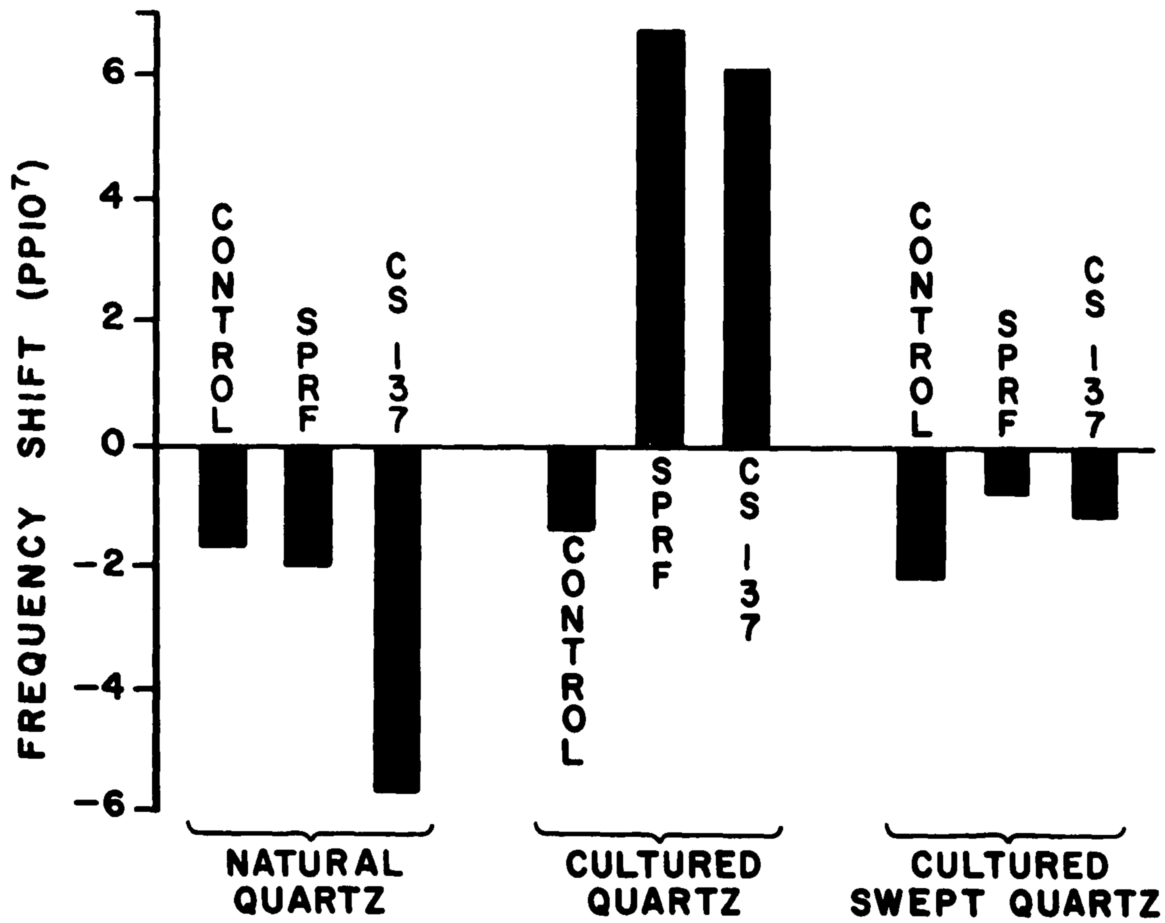

Figure 23. Summary of the effect of gamma radiation on 16 Mc resonators of various types of quartz (γ dose: 10^4 rads).

exposed to the Cs-137 source; resonators of swept cultured quartz were little affected. Resonators of cultured quartz, on the other hand, exhibited distinct positive shifts in all cases. The application of a correction factor based upon the average shifts experienced by the control units gave the following results:

Frequency Shifts (pp 10^7)

	Natural Quartz	Cultured Quartz	Swept Cultured Quartz
Exposed to SPRF	0.0	+8.1	-0.4
Exposed to Cs-137	-4.0	+8.4	+2.0

No particular evidence of variation due to type of metal plating, container, or bonding material were noted, probably because of the relatively small dosages and the relatively large frequency variation encountered as a result of temperature cycling. In fact, the effects of handling and thermal cycling in most cases have concealed the actual effects of irradiation. Only in the cases of Cs-137 irradiation of natural quartz and of both the SPRF and Cs-137 irradiation of cultured quartz were frequency shifts distinctly apparent.

These data agree essentially with those previously reported for quartz resonators irradiated with small dosages in the Cs-137 sources.

Aging rates of resonators exposed to radiation were little changed after a recovery period of about 30 days. Aging data of typical specimens are shown in Figures 24 and 25.

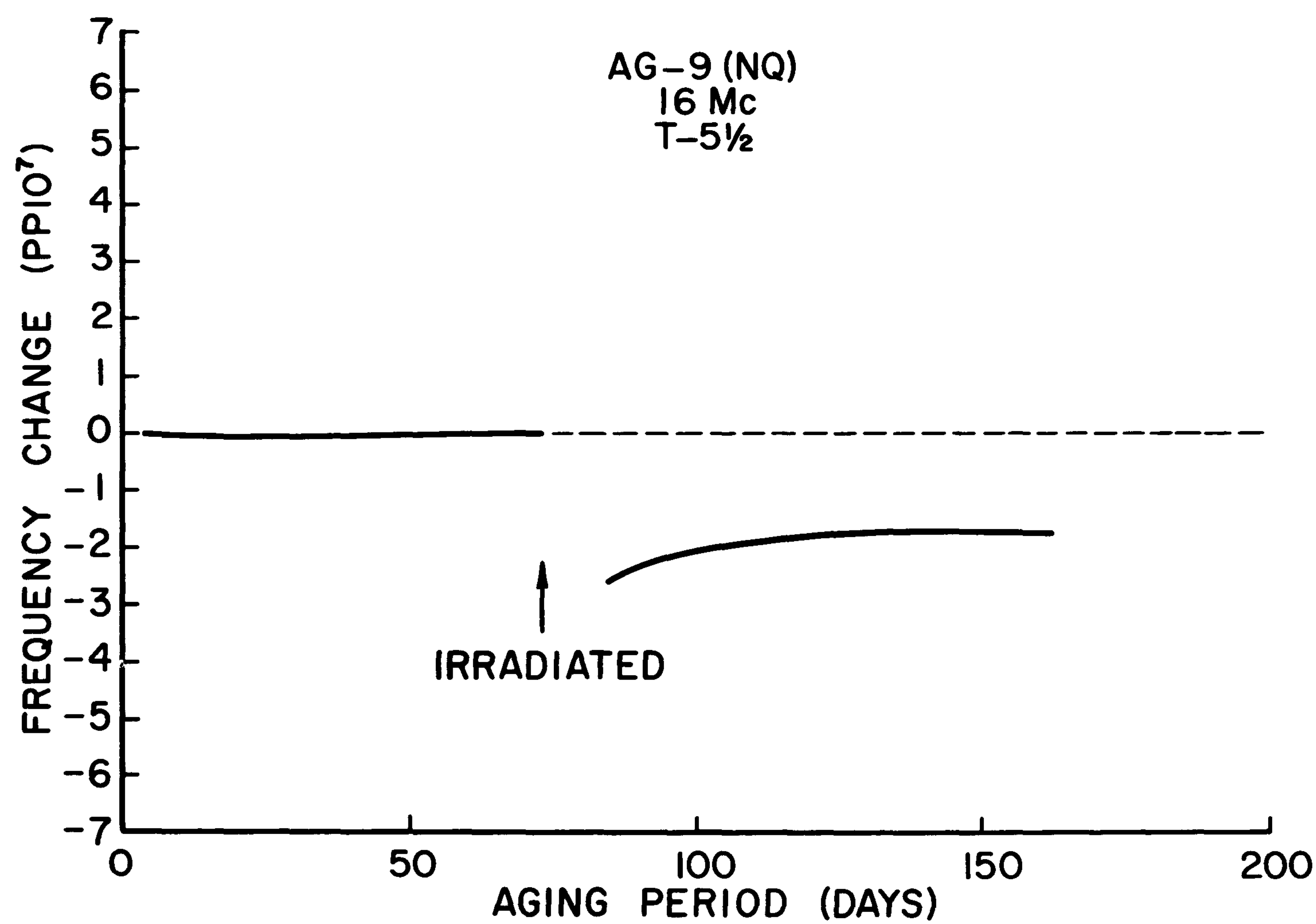

Figure 24. Aging of 16 Mc resonator Ag-9 (NQ) before and after gamma irradiation at SPRF (10^4 rads + 10^{13} nvt).

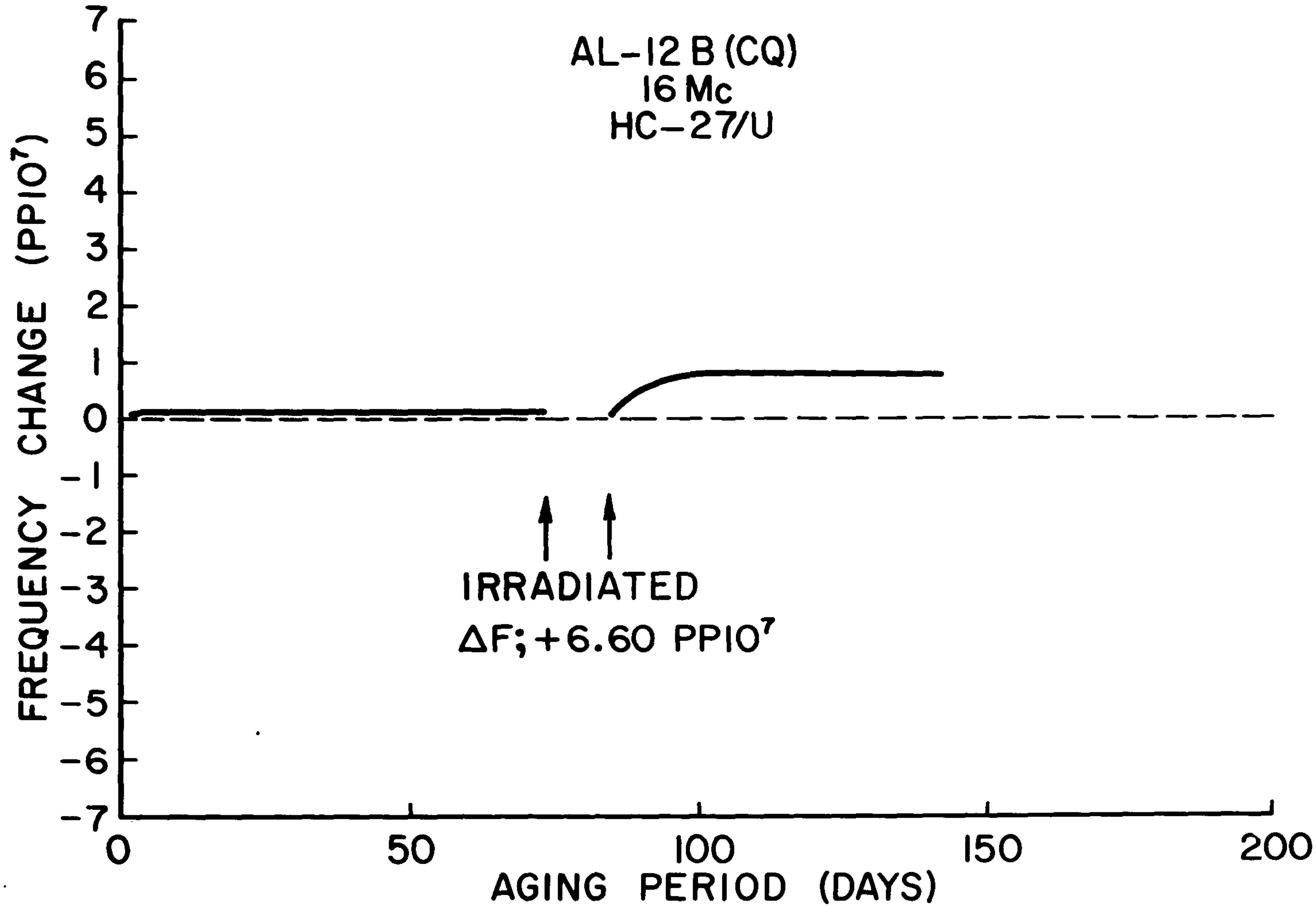

Figure 25. Aging of 16 Mc resonator Al-12B (CQ) before and after gamma irradiation at Georgia Tech (Cs-137, 10^4 rads).

C. STUDIES OF QUARTZ RESONATORS BY X-RAY DIFFRACTION METHODS*

1. Introduction

In our studies of quartz oscillators by x-ray means, two methods were employed: X-ray diffraction topography, and source image distortion. The topography apparatus, modeled after that described by A. R. Lang, and the SID apparatus, developed at Georgia Tech in 1962, are described in the Final Report, Contract No. DA-36-039-SC-87407, 15 February 1963.

An x-ray diffraction topograph gives, on film, a two-dimensional representation of the local perfection of a single crystal. Applied to quartz resonators then, this method displays the defect structure in the unit, i.e., the size and placement of defects occurring in the quartz. Here "defects" refers to any disruption of the perfection of the crystal lattice whether it is due to defects grown into the quartz (dislocation, impurity concentrations, etc.), damage of external origin (scratches on the surface from manufacturing processes, for example), or local strains associated with piezoelectric oscillation. The source image distortion (SID) technique yields the sum of the tilting of the Bragg planes and the gross distortion of lattice, as a function of position on the crystal. Tilting of the lattice planes is caused by gross distortion of the crystal (due to mounting supports for example), or by oscillation. In both methods only those characteristics which have a certain relationship to the particular Bragg planes used, are observed, so for a complete description of the quantity of interest, it is necessary that one use several different reflections (i.e., several different sets of Bragg planes).

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* Contributed by R. A. Young and C. E. Wagner, Diffraction Laboratories, Georgia Institute of Technology.

2. Results of Topography Studies

A discussion of the Lang topography studies in non-oscillating units is given in Report No. 6, Contract No. DA-36-039-AMC-02251(E), 15 August 1964. Examples of the various types of defects observed are presented, along with the pertinent electrical characteristics of the units shown.

Lang topography studies on the low frequency crystals are presented in Report No. 7, Contract No. DA-36-039-AMC-02251(E), 15 November 1964. The study of the SL-Cut, 455 Kc and 500 Kc units, using three different reflections, revealed that the SL-Cut is actually oscillating in a third order face-shear mode, rather than a fundamental length-width flexure, as previously suggested by others.* Thus, the mounting is in fact at a nodal position; it is not at an antinode as it would be were the mode a fundamental length-width flexure. It appears that the reason this 3rd order response at 455 Kc is so strong compared to the other responses lies in the choice of length-to-width ratio. End effects require the dimensions of the crystals to be other than exact multiples of the half-wave length involved. For the third order face-shear response, the width is a half-wave length and the length is three half-wave lengths plus an amount necessary to satisfy the requirements of the end effect.** The lowest frequency response found for the 455 Kc and 500 Kc crystals was about 195 Kc; topographs show that this is also a face-shear mode. At this lowest frequency the resistance is

* Report on a New Quartz Piezoelectric Element, the SL-Cut Vibrator. Prepared by Crystal Engineering Branch, USAF Standards Calibration and Certification Division, Directorate of Maintenance, Dayton Air Force Depot, Gentile Air Force Station, 26 October 1960.

** Because of anisotropy in the velocity of propagation and/or different end effect requirements, a half-wave length in one direction need not be the same size as a half-wave length in another direction. Thus, three half-wave lengths plus end effects is 10 mm in the X-direction for an SL-Cut, while one half-wave length plus end effects in the Z' direction is 4 mm.

about 50,000 ohms and both the frequency and resistance are notably drive sensitive. The motion can be simply represented as square, face-shear block, with large rectangular sections of extra material that follow the motion of the main block, attached on two sides. This extra matter is thought to be the cause of the unusually high resistance and drive sensitivity.

Some of the first topographic studies were concerned with the occurrence of electrical (Dauphiné) twinning and its effect on oscillation (Reports No. 3 and 4, Contract No. DA-36-039-AMC-02251(E), 15 November 1964). The relatively high incidence of twinning among some of the 16 Mc resonators (those prepared for the radiation experiment and mounted in the HC 27/U glass container) indicated that units of cultured swept quartz, or of high frequency, were more readily twinned than were units of natural quartz, or of low frequency. It appears that, when a unit becomes twinned, the twinned region extends throughout the thickness of the unit. Thus the thinner (higher frequency) units twin more readily than do the thicker ones. Different impurity and/or defect concentrations may account for the higher incidence of twinning in swept cultured quartz.

Twinning near the bonds of resonators fabricated in the HC 27/U glass containers at Georgia Tech has been observed in a number of instances. Commercial units were examined and three were found to be twinned in the lower portion of the plates. It is evident that twinning of the quartz during sealing in the HC 27/U glass containers is a fairly common occurrence.

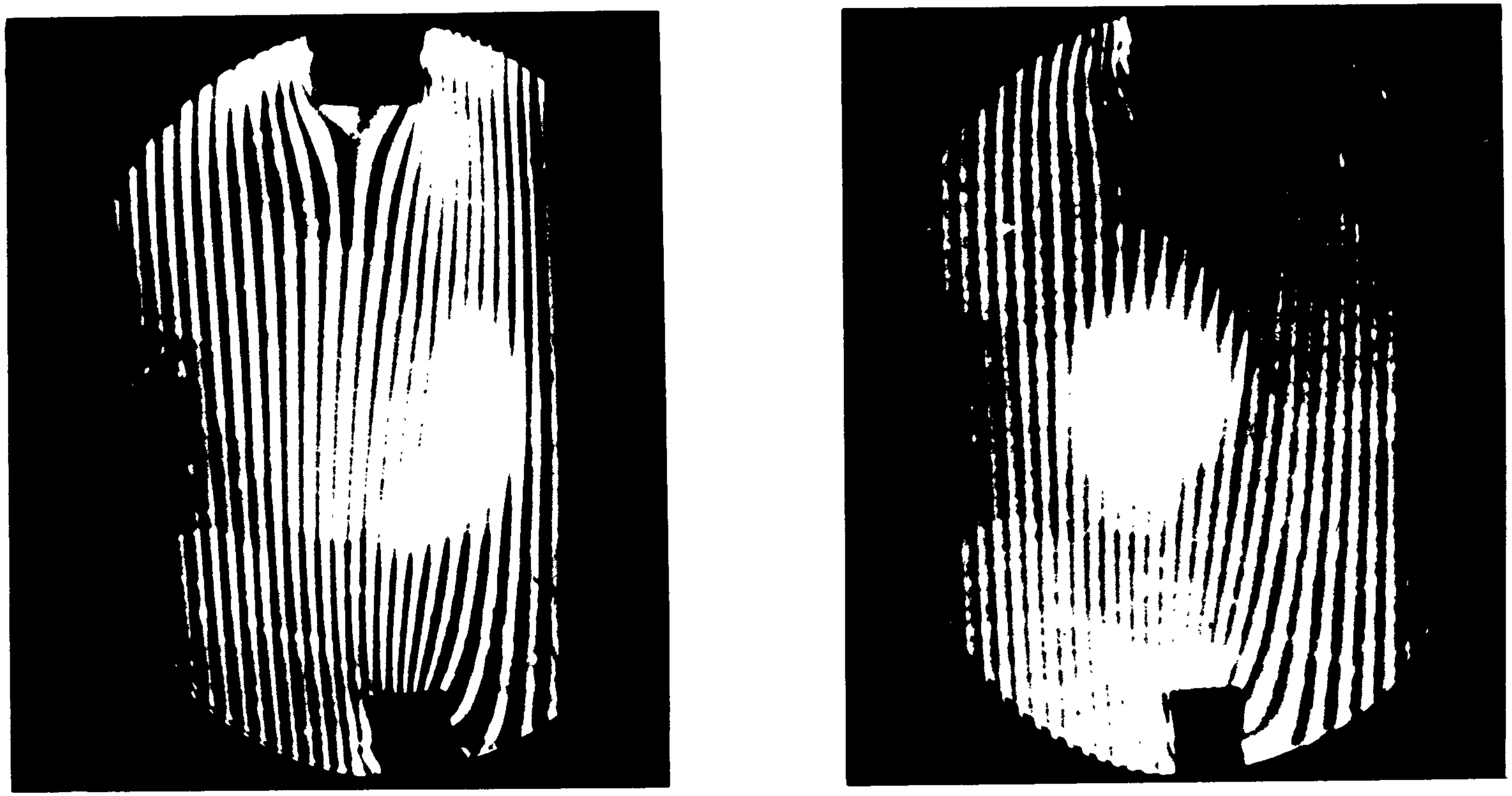
When a twin occurs in the region of oscillation, the effect is dramatic. The twinned region effectively has the negative of the rotation angle of the rest of the quartz, so the frequency is very different for this region.

Figure 26A, of 16 Mc unit Au 31, shows the oscillation pattern at 16 Mc; Figure 26B shows the same unit oscillating at 23 Mc. Figure 27 shows the twinned and untwinned regions. Another 16 Mc unit with a very similar twinning in the oscillation zone give a temperature versus frequency curve without a turnover point for the 23 Mc frequency. This curve matched rather well the temperature coefficient of frequency which might be expected if the angle of cut of a Y-cut crystal shifted from about + 35° (AT-Cut) to about - 35°. Finally, the frequency constant for this - 35° cut agreed reasonably well with the actual frequency of about 23 Mc.

Figures 28 and 29 show resonator Au-6B stationary and driven respectively. Here a feature which appears to be a crack leads directly into the oscillating region of the crystal, and distorts the distribution of activity. Note that the strain, and hence amplitude of displacement, is greatest near the crack.

A $2\bar{1}0$ diffraction pattern of unit A-8 is shown in Figure 30. Since there was some probability that much of the defect structure was due to surface damage incurred during preparation, the unit was etched in an ammonium bifluoride solution for 60 hours. The $2\bar{1}0$ pattern made after this etch is shown in Figure 31. Thus, it is seen that a considerable amount of surface damage may (and, no doubt, usually does) occur during the manufacturing process.

Topographs of the low frequency units show that, in general, the quartz used in these resonators is of lower quality than that used in the higher frequency units. The rough edge treatment given to these low frequency units



A. FUNDAMENTAL
16 MC/SEC

B. "SPURIOUS"
23 MC/SEC

Figure 26. X-ray SID patterns of 16 Mc Unit Au-31 oscillating at 16 and 23 Mc, ($2\bar{1}0$ reflection.)

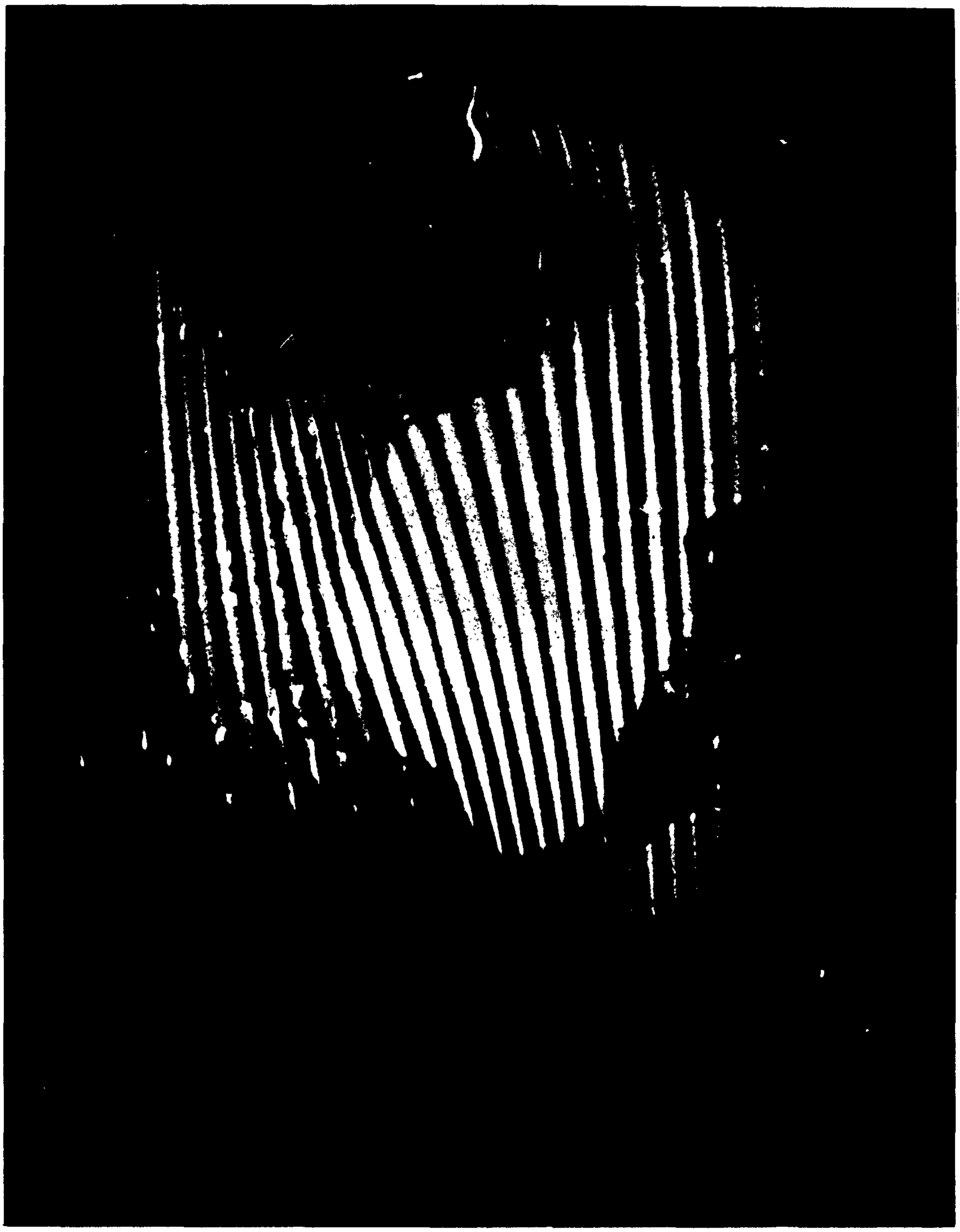


Figure 27. X-ray diffraction SID pattern of Au-31, not oscillating, ($0\bar{2}1$ reflection.)

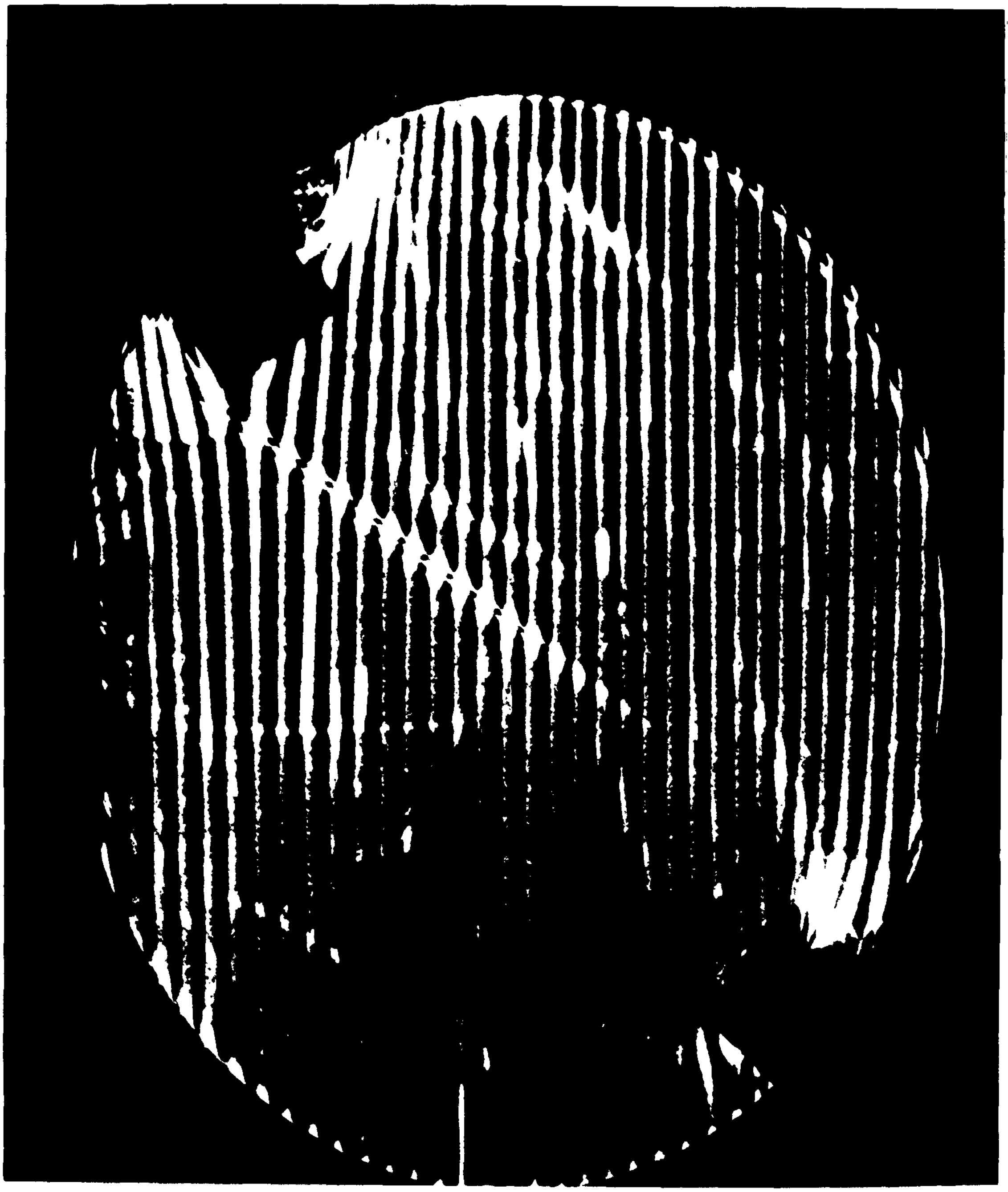


Figure 28. X-ray diffraction SID patterns of 16 Mc resonator Au-6B exhibiting defect running into central zone of crystal. Undriven.

Figure 29. X-ray diffraction SID patterns of 16 Mc resonator Au-6B exhibiting defect running into central zone of crystal. Oscillating at 3rd mode.

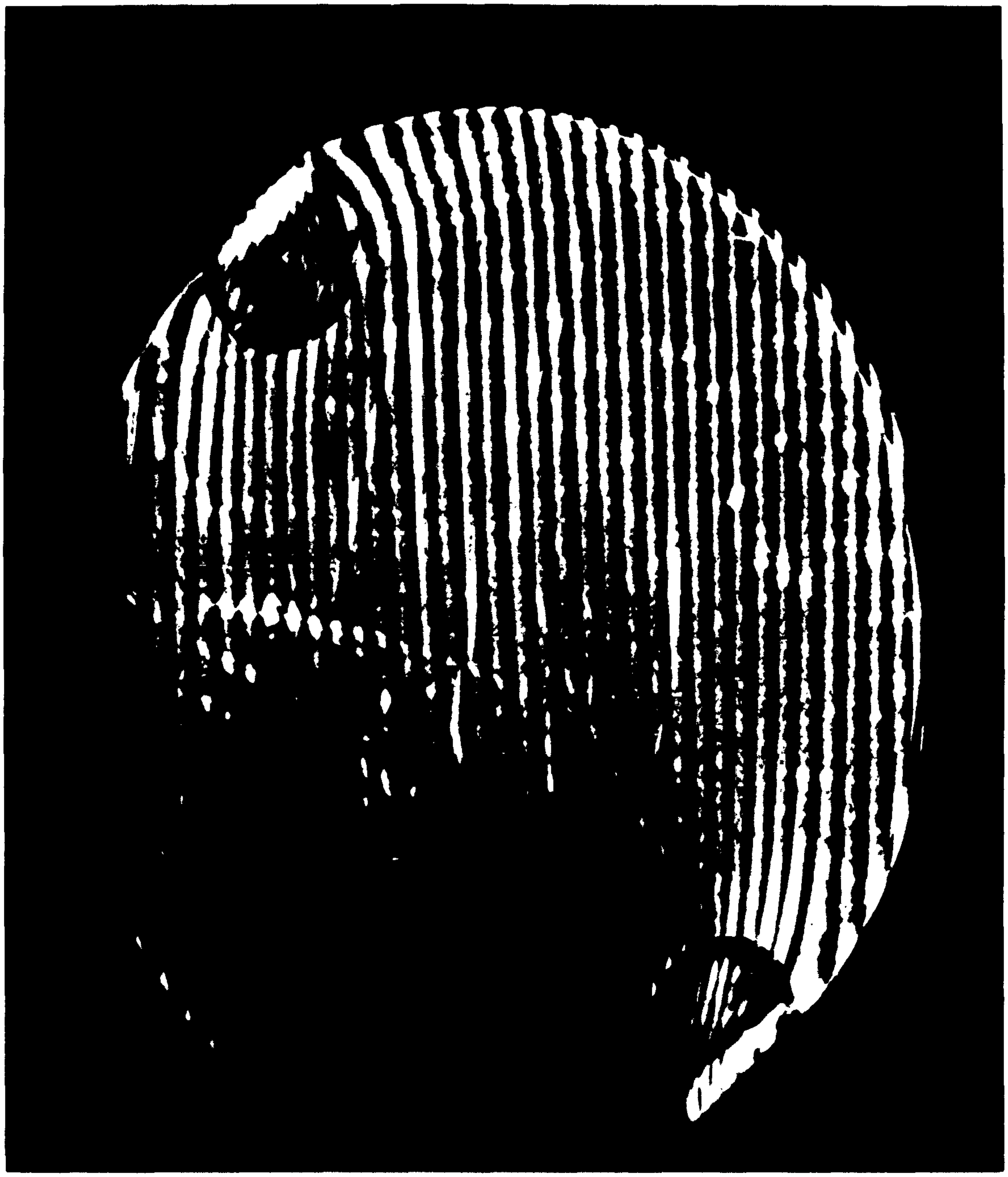


Figure 30. X-ray diffraction SID pattern of 10 Mc resonator A-8 before etching, ($2\bar{1}0$ reflection.)

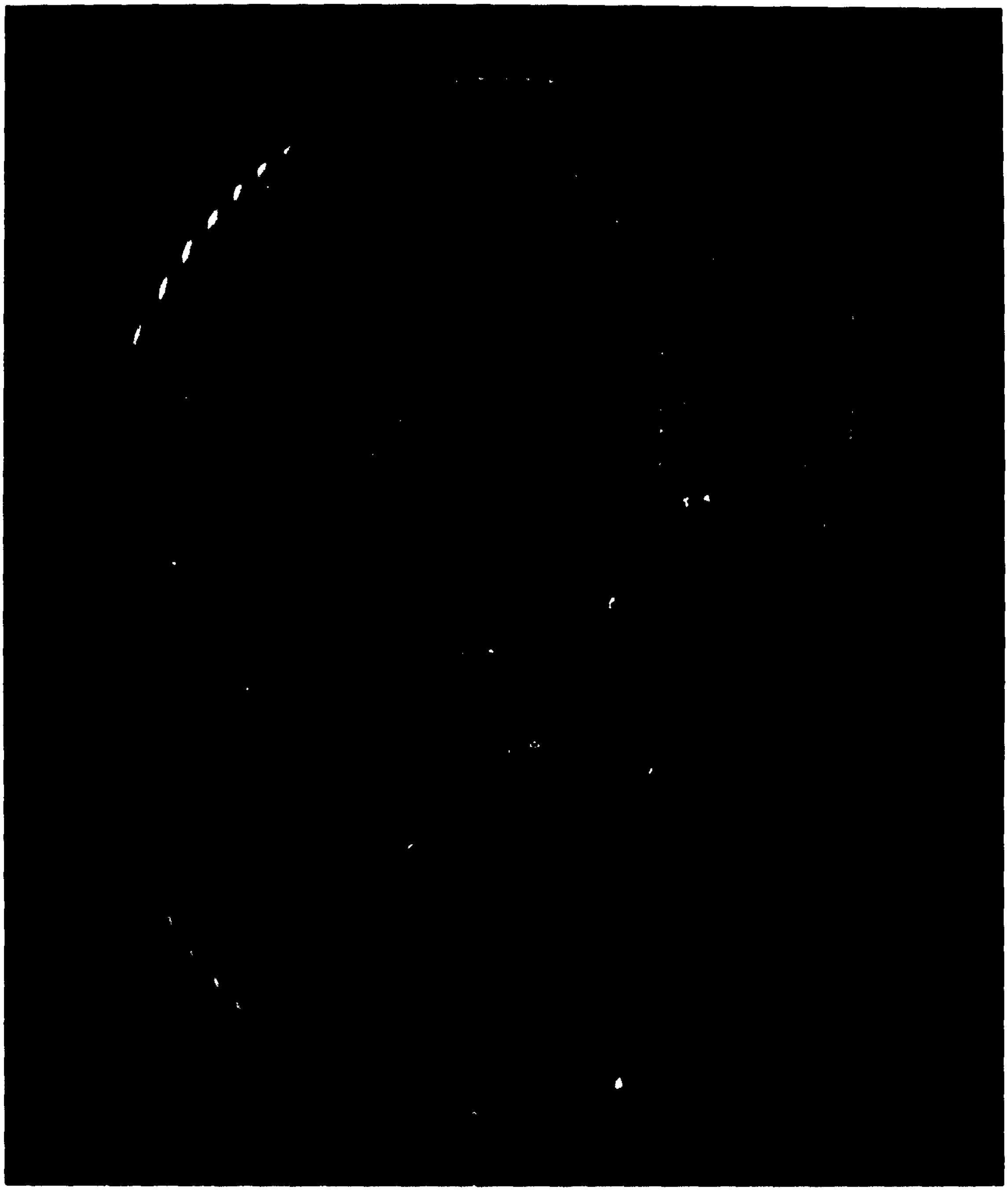


Figure 31. X-ray diffraction SID pattern of 10 Mc resonator A-8 after etching, ($2\bar{1}0$ reflection.)

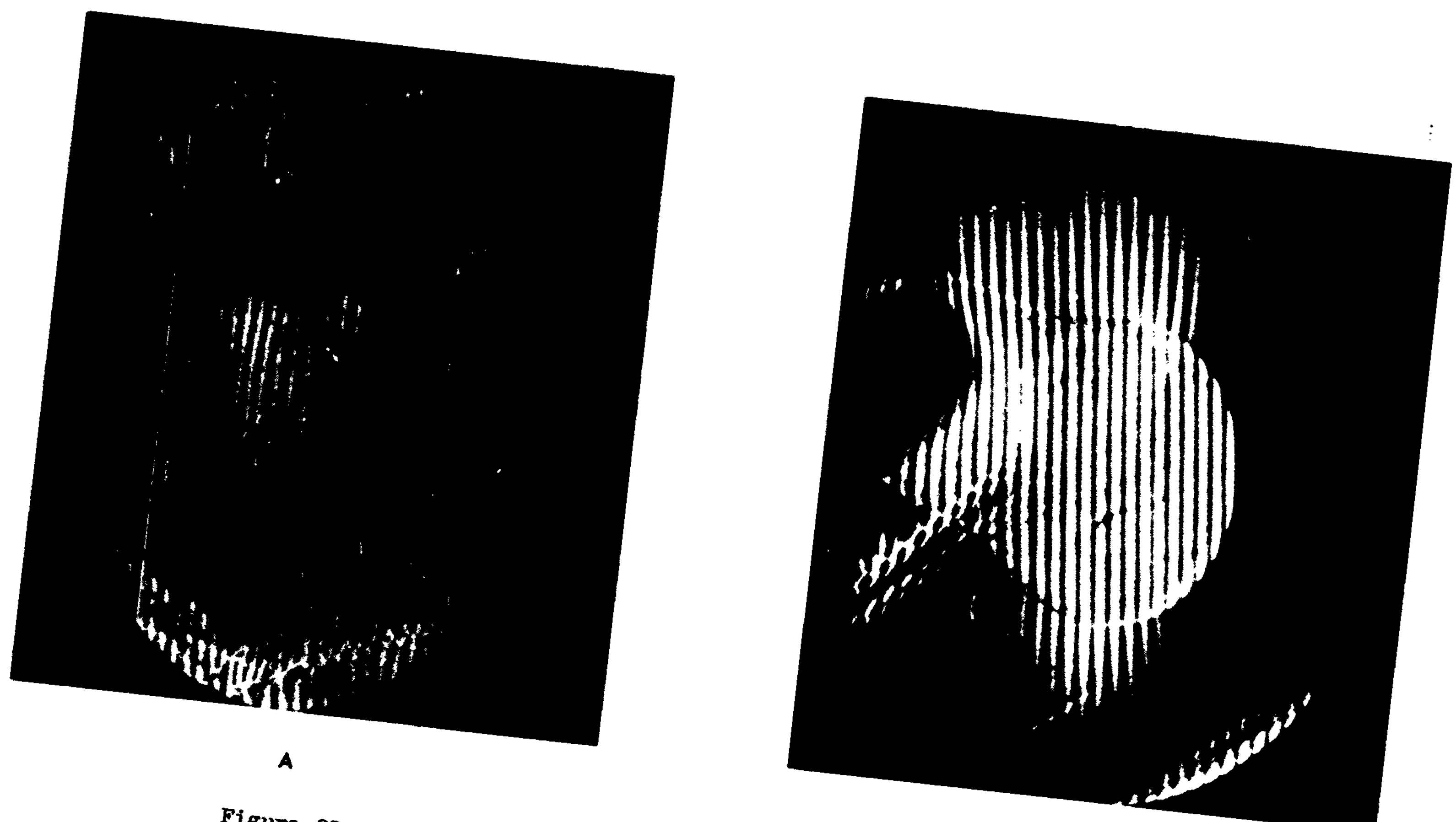
as a frequency adjustment method is apparent in the topographs. It is suggested that this rough treatment may be responsible for some of the poorer aging characteristics.

3. Source Image Distortion Studies

A discussion of the origin of tilt and strain information by the source image distortion (SID) method is given in Report No. 7, Contract No. DA-36-039-AMC-02251(E)., 15 November 1964. A detailed analysis of the relationship between displacement of the Soller slit images and angular deviation in the crystal is given in Report No. 4 of the same contract, 15 February 1964.

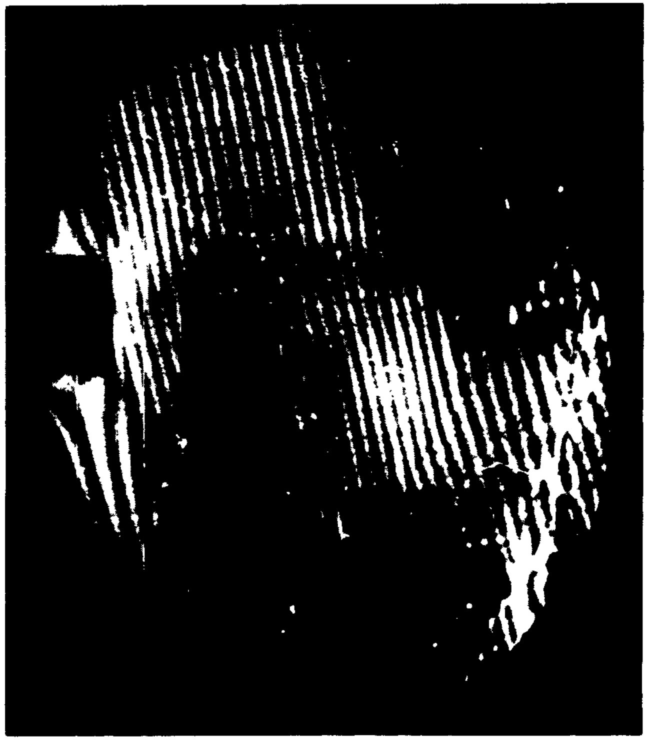
Distortions due to mounting have been observed in the great majority of the resonators examined, but no definite correlation between distortion and aging has been found, not even when the relationship between the X-axis and the bending direction was considered.

Because of the strain often observed at the edge of the plated region, an experiment was conducted to see how plating one side of a quartz blank would affect its curvature. SID patterns of several units were made before and after plating. A thin layer of nickel was sputtered on to the specimen and was followed by successive depositions of electroplated nickel. Figures 32 and 33 display the results of two such experiments. The intensity variation and curvature of the lines show that in both instances a small amount of strain was produced by the initial sputtered film of 600 Å, but whether this was caused by the sputtering action or the presence of the film is not yet known. When 16,000 Å of nickel was electroplated over the initial 600 Å, the blank became more distorted (Figure 32). After the addition of 33,000 Å

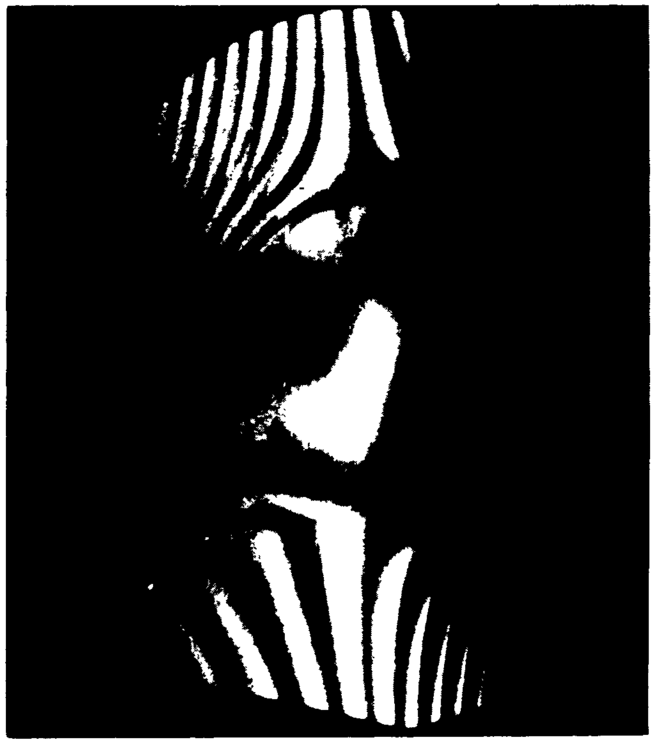


A B

Figure 32. X-ray SID patterns of a 20 Mc quartz wafer: (A) plated with 600 Å sputtered nickel and (B) with an additional 16000 Å of electroplated nickel.



A



B

QUARTZ BLANK PLATED ON ONE SIDE

Figure 33. X-ray of SID patterns of a 20 Mc quartz wafer: (A) plated with 1000 Å of sputtered nickel plus 1000 Å of electroplated nickel and (B) with an additional 31000 Å of electroplated nickel.

to another specimen (Figure 33), the quartz plate resembled a small concave mirror with a radius of curvature about 25 cm. Thus it is seen that plating, and/or the plating process, produces a strain on the quartz blank even with relatively thin platings, and often produces extreme strains with very thick films.

Oscillation, also causes tilting of the lattice planes, but only the component of the tilt about an axis perpendicular to the plane of incidence will show in a SID pattern. As one result, for a mode which produces no detectable tilting for the reflection used, coupling to modes which do produce tilting is immediately evident. Some SL-Cuts offer an example. Figure 34 is a $2\bar{1}0$ SID pattern of the principal mode of C2-455. The underlying topographic information shows it is coupled to at least one other mode. Figure 35 is a similarly made $2\bar{1}0$ SID pattern of another 455 KC unit, but in which the same coupling among modes does not occur. It is notable that in this latter, pure mode case, source image distortion is also absent.

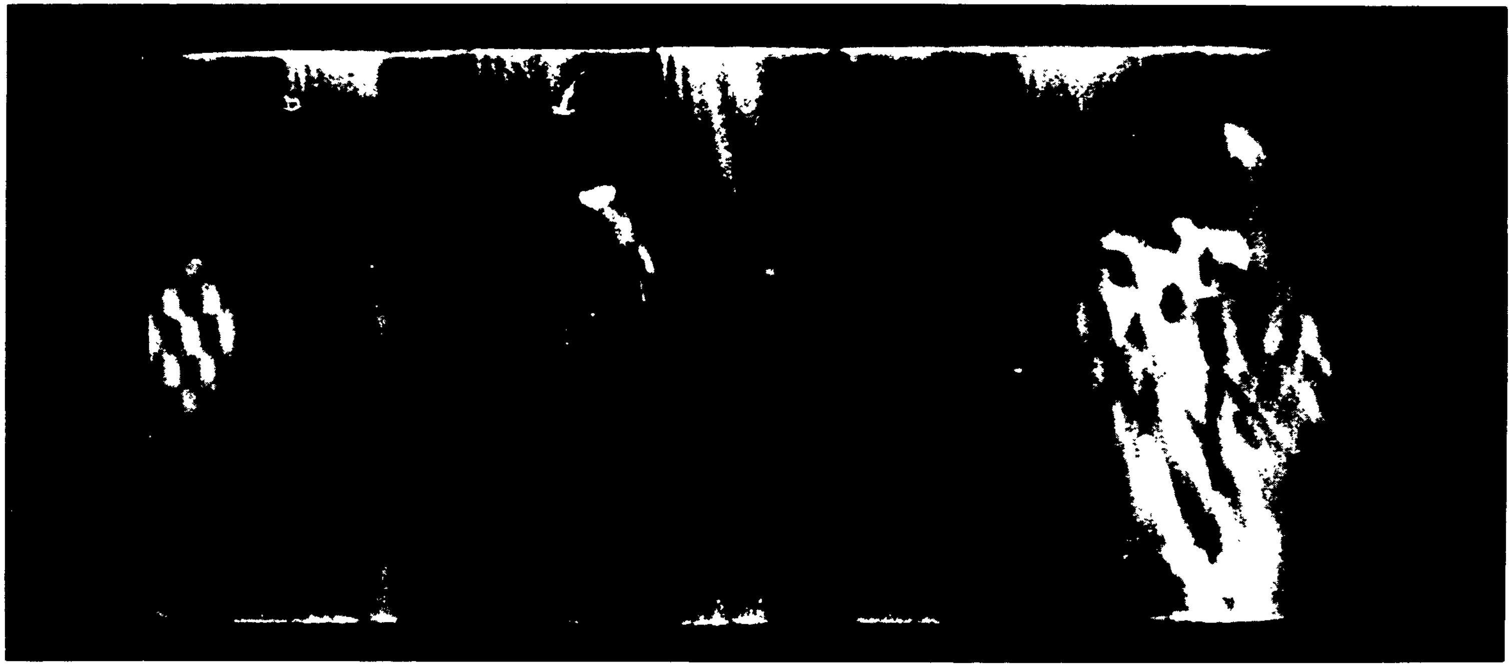


Figure 34. X-ray diffraction SID pattern of 455 Kc resonator C-2 exhibiting source image distortion due to coupled mode, ($2\bar{1}0$ reflection.)

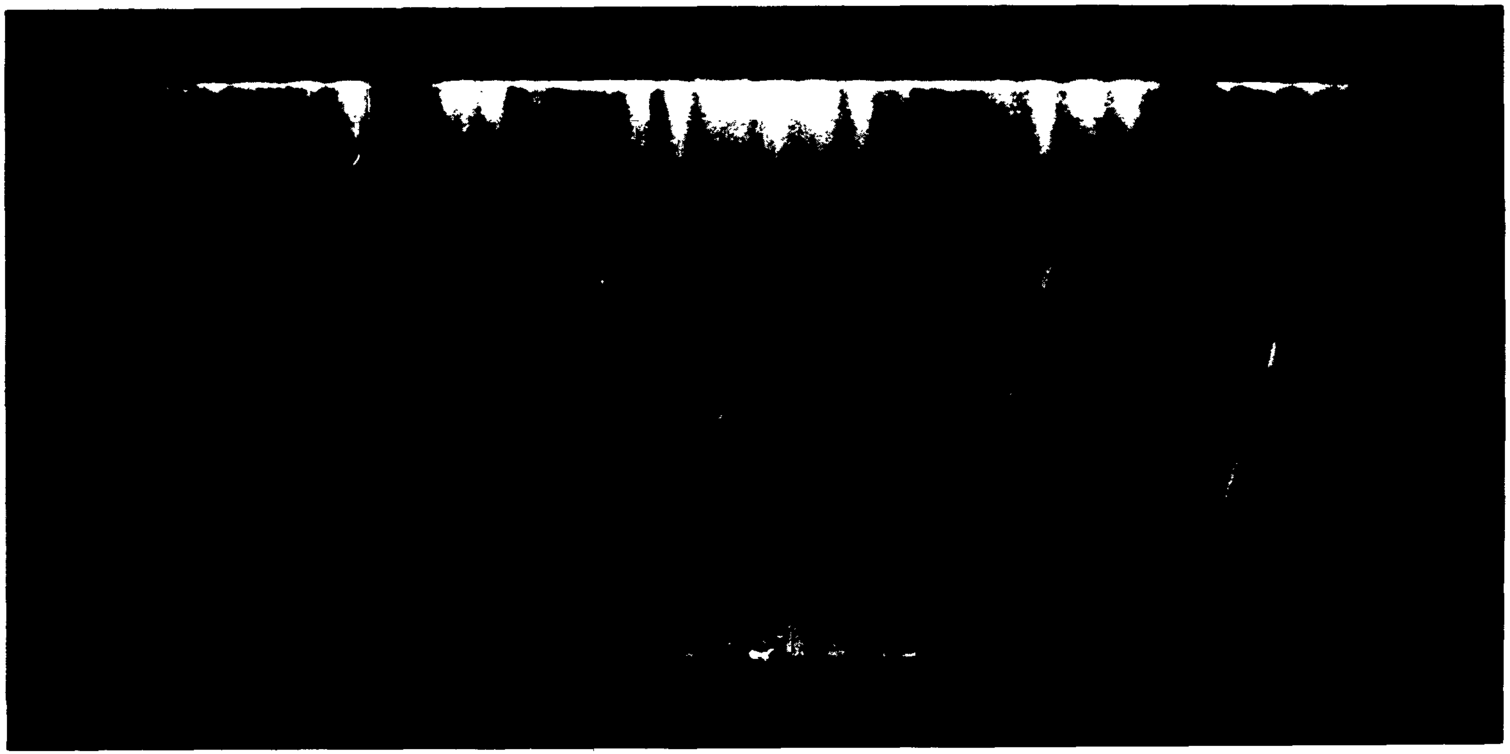


Figure 35. X-ray SID pattern of 455 Kc unit C-3 oscillating at 8.0 mw drive, ($2\bar{1}0$ reflection.)

V. CONCLUSIONS AND RECOMMENDATIONS

An extensive survey of the aging of quartz resonators of fundamental frequencies of 100, 250, 455 and 500 Kc, 3 Mc, 10 Mc and 16 Mc has been made. Although only 46% of the low frequency units were able to pass the initial acceptance test of $< 5 \times 10^{-6}$ in the first 30 days only 3/47 failed the subsequent requirement of $< 2 \times 10^{-6}$ per 30 days thereafter resulting in a reliability of 94% after 6 months. High positive aging rates initially appeared to be associated with strains introduced during fabrication and mounting. Abrasion of edges for frequency adjustment, separation of plated electrodes by airbrasive methods, silver spotting and soldering procedures, internal defects, and strained mounting assemblies, all seem to play a part in high initial positive aging vectors.

A comparison of the aging rates of 3 Mc AT-Cut resonators constructed of natural, swept natural cultured and swept cultured quartz gave some dispersion in initial aging rates. After 20 weeks the average aging rate of all units except the cultured quartz was $< 3 \times 10^{-9}$/week and the latter was about 1×10^{-8}/week. These data were taken for the 3rd inharmonic response in Z' (113 mode) at 3.22 Mc instead of the (111) mode at 3.00 Mc. A comparison of the aging rates at the two modes showed a somewhat higher degree of dispersion of the rates measured at the 3.22 Mc response than at the 3.00 Mc response because of a higher temperature coefficient of frequency (1.2 ppm for natural quartz) at 85°C for this response. The validity of the comparison is thus in doubt.

A mode study of these units, made by x-ray diffraction methods as a result of the problems encountered, delineated oscillatory zones for a number of

harmonic and inharmonic responses and supported earlier work performed by powder, potential probe, and theoretical methods. It also revealed the potential of the x-ray diffraction method for studies of this nature.

Aging studies of 10 Mc resonators constructed for reliability measurements gave a yield of 80% of units fabricated where preferred methods were adhered to, but only 64%, when one batch of units mounted in the HC 27/U glass unit and bonded with duPont 5504-A Cement, was included in the yield calculation. Reliability performance of 27 units for 11 months was 100% but after that 2 units failed giving a reliability of 92.6% at the end of 14 months. Aging analyses of many units by x-ray diffraction methods and all units by visual methods revealed a high incidence of both surface and internal flaws or defects. However, it does not appear possible to date to predict, except in rare instances, probable failures. Four of 10 failing units disassembled, etched, and remounted gave remarkably stable performance subsequently in spite of severe internal banding depicted by x-ray diffraction methods. Therefore, the importance of the surface flaws is great, as has been pointed out by "Smagin" and others.

Aging studies conducted with similar 10 Mc resonators to evaluate the bonding cements duPont 5504-A, duPont 5605, Bondmaster (M 640), Bakelite, and Pyroceram (95) revealed that the first three were almost equal in performance where normal temperatures were encountered, whereas Bakelite and Pyroceram were much more sensitive to the surface condition of the resonators. An additional etch step, better clip alignment, and narrow plated tabs were resorted to to improve performance of these latter units. The greater elasticity of these cements seemed to transmit acoustic energy to the mounting wire

which then became a part of the vibrating system. Oscillation in the tab zone was demonstrated by x-ray diffraction patterns. Upon temperature cycling these same units to 300°C for five minutes shifts in frequency from $+ 48 \times 10^{-7}$ to $- 98 \times 10^{-7}$ were observed. However, the average shift with the exception of the earliest 5504-A cement group, was about 8×10^{-7}. Aging rates for the better units were little changed except for short stabilization periods occurring within the first 30 days. Bondmaster proved to be the least affected cement but etched units utilizing du Pont 5504-A were as good or better. All of the cements were acceptable with regard to the aging requirement of $< 1 \times 10^{-7}$ per week; and there were not great differences in performance during the 300°C temperature cycle, Pyroceram and Bakelite, however, appear unsuitable without the etch step; and apparently resonators mounted with any of the cements will benefit from the suggested final etch step before plating.

Drive sensitivity studies made in conjunction with the cement evaluation studies revealed that units with high drive sensitivity were generally poor with regard to aging. In particular the etching step previously described, was found useful in reducing drive sensitivity and aging.

Exposure of 96 16 Mc resonators divided equally among natural, cultured and swept cultured quartz to irradiation doses equivalent to 10^4 rads of gamma radiation produced by either a Cs 137 source or at the SPRF resulted in relatively small changes in frequency of only a few parts in 10^7. Except in the case of the cultured quartz, and of natural quartz exposed to the Cs 137 source, changes were little greater than those of control units experiencing the same transportation and thermal cycling conditions but not irradiated.

However, the superior stability of the swept cultured specimens in radiation environments was discernible and confirmed earlier measurements at more severe dose levels.

X-ray diffraction techniques of examining quartz resonators have revealed many conditions conducive to aging. For low frequency resonators these include internal defects, surface defects, grinding strain, bonding strain, mounting strain, and strain induced by airbrasives used in plating separation. For AT-Cut resonators, surface scratches, internal defects, twinning, bonding strain, and edge grinding strain have been made visible. In oscillating crystals active zones have been displayed and examined; and thus have been made available for mode and aging analyses studies. The normal mode of operation of SL-Cut crystals has been shown to be third order face shear and the vibrational zones of several inharmonic responses of 3 Mc resonators have been exhibited. Methods of calculating distortion, strain, and vibrational amplitude have been outlined and mode analysis methods have been developed. These various sources of information have rendered a great service in a better understanding of the aging problem.

An investigation of the reduction of the aging of low frequency resonators by eliminating or reducing some of the present features which have been indicated as possible contributors to aging is recommended. Such measures as polishing edges, and thermal compression or ultrasonic bonding of leads have been suggested. Mounting materials and systems should also be studied. For AT-Cuts an evaluation of the effects on aging of thermal compression or ultrasonic bonded leads and cold welding of containers appears as an appropriate next step. Performance of parallel excited elements is also of interest. Employment of x-ray diffraction methods is recommended for aging and mode analyses studies.

VI. PERSONNEL

Persons employed on this research and the approximate hours worked by each during the period 15 February 1963 to 15 February 1965 are stated below.

Individual	Title	Hours
R. B. Belser*	Research Associate Professor, Project Director	2141
R. A. Young*	Research Professor of Physics and Research Associate	386
A. L. Bennett*	Research Professor of Physics	418
W. H. Hicklin*	Assistant Research Engineer	3602
J. C. Meaders*	Research Assistant	3589
James O. Darnell	Research Assistant	1120
Carroll Shirley	Technician	2560
Charles E. Wagner* and other Grad. Assts.	X-ray	1661
T. L. Spradlin and other Grad. Assts.	Electronics	752
J. R. Miller*	Student Assistant	1035

The principal personnel assigned to the work (the first five listed) were associated with the research during the entire period. Changes in the categories of research assistant, graduate assistant, technician, and student assistant occurred from time to time and were duly reported in appropriate Quarterly Reports. The persons whose names are marked with an asterisk were with the project during the final year of the work.

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CONTRACTOR: Georgia Institute of Technology DATE: 15 February 1965

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This contract is supervised by the Solid State and Frequency Control Division, Electronic Components Department, USAELRDL, Fort Monmouth, New Jersey. For further technical information, contact the Project Engineer, Mr. Patrick E. Mulvihill, Telephone 535-2475 (New Jersey Area Code 201).

AD ______________________ Accession No. ______________
Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia, QUARTZ CRYSTAL AGING EFFECTS, R. B. Belser and W. H. Hicklin.

Report No. 8 (Interim Report), 15 February 1963 to 15 February 1965, 83 pp, 35 Illus. Signal Corps Contract No. DA-36-039-AMC-02251(E) Unclassified Report.

The purpose of this research is to improve the aging and reliability of quartz resonators.

Approximately 325 quartz resonators have been fabricated or purchased and measured for aging and reliability at 85°C over periods up to 14 months. These have been divided among low frequency (100 to 500 kc), 3 Mc, 10 Mc and 16 Mc resonators and among natural, cultured, and electrolytically swept natural and cultured quartz. Data accumulated by electrical measurements and by visual and x-ray diffraction methods have been analyzed in order to determine mechanisms responsible for the principal aging vectors observed. Measured reliabilities are reported.

Of 96 low frequency resonators only 46 percent passed the initial aging requirement of < 5 ppm during the first 30 days. Three of these failed the subsequent requirement of < 2 ppm each 30 days thereafter giving a reliability of 94% for a 6 month period. Analyses by x-ray diffraction methods revealed strains associated with the quartz blank fabrication and mounting methods. Edge grinding, solder spotting, plating separation by airbrasive, quartz defects, and strained mounts, all appeared as possible contributors to high positive aging rates.

A comparison of the aging rates of 3 Mc resonators constructed of natural, natural swept quartz, cultured and cultured swept quartz was made, but inadvertently at the third inharmonic response in z' rather than at the fundamental. At this response, after 20 weeks, rates were $< 3 \times 10^{-9}$/wk for all except the cultured quartz which remained slightly $> 1 \times 10^{-8}$/wk. A comparison of the aging at the fundamental (3.00 Mc) and third inharmonic (3.22 Mc) responses revealed that the 3.22 Mc response was more temperature sensitive (about 1.2 ppm/°C) than the 3.00 Mc response but aging rates were little different over a 15 day period.

UNCLASSIFIED

1. Quartz Crystal Aging Effects
2. Signal Corps Contract No. DA-36-039-AMC-02251(E)

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Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia, QUARTZ CRYSTAL AGING EFFECTS, R. B. Belser and W. H. Hicklin.

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UNCLASSIFIED

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2. Signal Corps Contract No. DA-36-039-AMC-02251(E)

Ten Mc AT-cut resonators, fabricated for reliability and cement bond evaluation studies, were examined. Of 27 units 100 percent reliability was maintained for 11 months, based on an aging rate of $< 1 \times 10^{-7}$/wk. Two units became erratic and at 14 months reliability was 92.6%. Aging rate for better units at this time did not exceed $\pm 1.2 \times 10^{-8}$/month Concurrently, of 68 10 Mc resonators, bonded with various cements and examined for cement bond evaluation studies, 86% and 91% respectively passed the initial and subsequent aging requirement of $< 1 \times 10^{-7}$/wk. After temperature cycling to 300°C frequency shifts up to 10×10^{-7} were common; however, 41% shifted $< 5 \times 10^{-7}$. Aging rates subsequent to temperature cycling were little changed. Bondmaster bonded resonators withstood the temperature cycling with the least frequency change; however, Pyroceram bonded units gave uniform frequency changes in a positive direction. Drive sensitivity was found related to aging and to resonator performance with various cements. Resonator etch techniques were developed which improved drive sensitivity, aging, and cement performance.

16 Mc AT-cut resonators fabricated, aged, and exposed to gamma radiation doses of 10 rads at Georgia Tech (Cs-137 source) and at SPRF exhibited frequency changes of a few parts in 10^{7}, of the order of magnitude of changes incurred by control specimens exposed to the same thermal and mechanical experiences. Elements of cultured quartz exhibited definite small positive shifts, however, and natural quartz revealed slight negative ones. The swept cultured quartz was least affected as reported in previous experiments.

X-ray diffraction investigations of quartz made concurrently with aging studies have revealed strains due to edge grinding, scratches, solder spotting, plating separation, twinning, bonding cements, metal films, internal defects, and twisting due to mounting systems. These have been associated where practicable with aging, principally among the low frequency units. For the AT-cut units the relation is less substantive but exists in some cases. Methods of x-ray diffraction analyses of vibrating modes of quartz crystals have been discussed and the normal mode of oscillation of the SL-cut crystal has been shown to be 3rd order face shear.

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